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EXERCISES IN
PHYSICAL CHEMISTRY

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EXERCISES IN
PHYSICAL CHEMISTRY

BY

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AUTHORISED TRANSLATION

BY

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AUTHOR'S PREFACE TO THE GERMAN EDITION

It may seem questionable whether there is any necessity for a new book on Practical Physical Chemistry, in view of the well-known books of Kohlrausch, Ostwald-Luther, and Wiedemann-Ebert. Nevertheless, my own teaching experience and those of my colleagues have proved to me that these books, though good in themselves, contain either too much, or too little, for the beginner. Consequently in this little book I have tried to provide something for the elementary student who is commencing to study the subject, for that purpose assuming as little previous knowledge as possible. I have tried to connect the training in experimental method with the theoretical conclusions derived from the results, and further to train the student to deduce his results correctly, and to comprehend the inner relationships between the data obtained from entirely different experiments.

This explains the reason that certain standard substances (as sodium chloride, silver nitrate, silver chloride, chloroform, and benzene) are suggested for use in exercises on quite independent work. I have laid special stress on the practical application of physical-chemical methods in quantitative analysis, and in the determination of the constitution of compounds. I have, however, not treated of electrolysis and spectrum analysis, since the student is supposed to be acquainted with these subjects from the course of analytical chemistry.

The book is in great part based on the *Kleine Practikum* of physical chemistry, which was arranged by Professor Nernst, in Göttingen and Berlin Universities, and which I had to conduct in Berlin.

The student is advised to read the first chapter thoroughly before proceeding to the actual measurements, since the subjects discussed in it relate to all the subsequent experiments. In order to make the book as compact as possible, lengthy deductions and complicated tables have been omitted. Further details on such fundamental physical measurements as weighing and different methods of calibration must be sought for in larger text-books of practical physics. More details concerning the theoretical deductions will be found in the well-known text-books of physical chemistry, especially in that of Nernst. The actual experimental results can be controlled by consulting one of the large volumes of tables. The books of Kohlrausch, Ostwald-Luther, Nernst, Ostwald, and Landolt-Börnstein are certain to be found in the library of every chemical laboratory.

In order to recall the fundamental laws to the memory of the beginner, qualitative experiments are described—in small type—at the beginning of most of the chapters; the greater part of these have been tested as lecture experiments.

Perhaps I may be reproached with the fact that I have treated many sections—*e.g.*, that on thermochemistry—with an undoubted preference, and more detailed consideration than others. But thermochemistry and thermodynamics are the framework of the whole of physical chemistry. Moreover, it is open to all to select from the exercises according to the time at their disposal.

The illustrations, which are reproduced from my sketches, are designedly quite simple and schematic diagrams, such as are drawn on the blackboard in a practical course. My thanks are due to my colleagues for all suggested alterations and additions.

W. A. ROTH.

GREIFSWALD,
December, 1906.

TRANSLATOR'S PREFACE

The same reasons which made the publication of this volume desirable in Germany hold with equal force for the English edition.

The book has been revised throughout by the author, who has made numerous additions. The most important is that dealing with oxidation and reduction cells, and the mechanism of current production (Chapter XI.); others are concerned with Lippmann's electrometer, the electrical measurement of solubility, polarimetry, etc.

I have added a short chapter on the construction and use of the thermostat, and an appendix on the use of the electroscope in radio-active work.

The illustrations have been redrawn, and a few new ones added where desirable.

I have pleasure in expressing my thanks to the author for his kindness in reading the proof-sheets. Dr. N. T. M. Wilsmore has also kindly read a part of the proofs. I am indebted especially to Dr. Otto Brill, who gave me considerable assistance with the translation.

January, 1909.

Phys. Chem. Institut,
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EXERCISES IN PHYSICAL CHEMISTRY

CHAPTER I

INTRODUCTORY

Methods of Calculation—Abbreviated Arithmetic.

Where the procedure of an experimental measurement is obvious, and the result is known approximately, it is advisable to make a rough calculation previously in order to select a suitable value for the variable, whatever that may be (*e.g.*, the weight or volume of the substance to be used in the experiment, the duration of a current, resistance, etc.). The arithmetic of such a calculation can be shortened greatly by devices such as neglect of quantities of the second order and use of round numbers.

From this point of view practice in mental arithmetic and ability to grasp rapidly a group of numerical terms cannot be valued too highly. The student should accustom himself, therefore, to calculate rapidly either mentally or at any rate without the use of logarithms, for which purpose the following simplifications will be found useful. Used with judgment, they can be employed in all calculations, however accurate.

If the quantities represented by Greek characters in the equations which follow are small in comparison with the others we can write

$$(1 \pm \alpha)^n = 1 \pm n \, . \, \alpha \, ;^*$$

---

[*] The degree of error introduced by this contraction is shown by the size of the terms omitted:

$$+ \frac{n\,(n-1)}{1 \cdot 2} \alpha^2 + \frac{n\,(n-1)}{1 \cdot 2 \cdot 3} \alpha^3 + \ . \ . \ . \ ;$$

in very rare cases the term in α^2 can also be introduced.

Some important examples are given :—
The expansion of a cube becomes

$$(1 \pm a)^3 = 1 \pm 3a.$$

Again,

$$\sqrt{1 \pm a} = 1 \pm \frac{a}{2}; \quad \frac{1}{1 \pm a} = 1 \mp a;$$

and similarly,

$$\frac{(1 \pm a)(1 \pm \beta)}{(1 \pm \gamma)(1 \pm \delta)} = 1 \pm a \pm \beta \mp \gamma \mp \delta.$$

The last example is applicable in all calculations.

If A and B are two numbers nearly equal in value, then

$$\sqrt{A B} = \frac{1}{2}(A + B).$$

This finds an application in double weighing. A square number can be replaced usefully, and without appreciable error by a product of two similar terms. Thus A^2 can be replaced as indicated :—

$$A^2 - a^2 = (A - a)(A + a);$$

again, $$\ln(1 + \delta) = \delta - \frac{\delta^2}{2}$$

(for applications see pp. 61 and 139).*

A logarithmic slide rule, about a foot in length, is recommended where greater accuracy is required. With some practice the error in using such an instrument does not exceed $\frac{1}{4}$ to $\frac{1}{8}$ per cent.; for all calculations in which logarithms can be used it is very convenient. Where logarithms are employed

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* These simplifications are illustrated in the following example. The molecular elevation of the boiling point, k, for acetone, can be calculated approximately and rapidly as follows :

As shown later (p. 40) we can write $k = \frac{R \times T_o^2}{q} \cdot \frac{1}{1000}$,

$R = 1{\cdot}985$, and for acetone $T_o = 273 + 56{\cdot}3$, $q = 125{\cdot}3$. Exact calculation gives $k = 1{\cdot}718$. Simplified methods allow the rapid calculation :—

$$R = 2 \text{ (approx.)}; \quad T_o^2 = 329{\cdot}3^2 = 333{\cdot}3 \times 324 = \frac{1000}{3} \times 324;$$

$$q = 125 = \frac{1000}{8};$$

therefore $$k = \frac{2 \times 1000 \times 324 \times 8}{3 \times 1000 \times 1000} = 16 \times 0{\cdot}108 = 1{\cdot}73.$$

Since R was taken as 2 an error of about 0·7 per cent. was introduced. This is corrected by subtracting 0·01; the result is 1·72.

four-place tables usually suffice. In such measurements as density or molecular refraction (see pp. 75 *et seq.*), where very great accuracy is desired, five-place tables must be used.

If a series of similar calculations has to be made, some special scheme should be drawn up and employed.

The physical-chemist employs as unit of mass not the gram but the *gram-molecule*; he expresses concentration in *normality* instead of in percentage.

Calculation of Average Value and of Error.

If a magnitude A has been determined n times, and all the n observations are of about the same degree of accuracy, then the most probable real value is the arithmetical mean $\Sigma \frac{A}{n}$. The calculation is simplified by selecting a whole number lying between the greatest and least values as a first approximation, from which the other numbers are each subtracted. The positive differences are added together, and also the negative differences; the totals are subtracted, the difference divided by n, and the result, according to its sign, is added to or subtracted from the whole number chosen.

Example.—The following resistances are observed :—252·0, 249·8, 251·3, 250·1, 248·5 Ω. Their differences from 250·0 are, respectively

$$\left.\begin{array}{lllll} +2{\cdot}0 & +1{\cdot}3 & +0{\cdot}1\,; & \text{sum} & +3{\cdot}4 \\ -0{\cdot}2 & -1{\cdot}5 & \phantom{+0{\cdot}1}\,; & \;\;,, & -1{\cdot}7 \end{array}\right\}\ \text{difference} +1{\cdot}7.$$

Therefore the true average value is

$$250{\cdot}0\ \Omega + \frac{1{\cdot}7}{5}\ \Omega = 250{\cdot}3\ \Omega.$$

In a series of values, if one shows a considerable divergence from the others, it is not permissible to reject it arbitrarily unless there is definite well-grounded suspicion regarding its correctness.

If different values are known to possess a different degree of accuracy, *e.g.*, when widely different quantities of a substance are used, or if in one reading the *end* of the measuring wire is used in the measurement of resistances, then different *weight* must be laid on these values; the more exact are multiplied by a factor corresponding to the degree of their accuracy, and the average value is determined from the numbers so obtained :—

$$x = \frac{n_1 A_1 + n_2 A_2 + n_3 A_3 + \ldots}{n_1 + n_2 + n_3 + \ldots}$$

Where in one continuous experiment a series of successive values are obtained, *e.g.*, in measurements of wave-lengths of sound in a Kundt's Tube in order to determine c_p/c_v (p. 68), it is easily seen that calculation of the simple average gives no greater accuracy than if the first and last values are considered. Hence, to make full use of the observations, some other method must be employed. Let there be n values measured, A_1, A_2, . . . A_n, so that the difference $(A_n - A_1)$ contains the sought-for value $(n - 1)$ times; therefore the factor proportional to the degree of accuracy of this value is $(n - 1)$; the difference $(A_{n-1} - A_2)$ containing the single value $(n - 3)$ times has similarly to be taken into consideration $(n - 3)$ times in determining the average. The value x, sought for, is accordingly :—

$$x = \frac{(n - 1)(A_n - A_1) + (n - 3)(A_{n-1} - A_2) + \ldots}{(n - 1)^2 + (n - 3)^2 + \ldots}$$

$$= 6\,\frac{(n - 1)(A_n - A_1) + (n - 3)(A_{n-1} - A_2) + \ldots}{n(n^2 - 1).}$$

It will be seen at once that it is advisable to take an even number of readings; otherwise the middle value will not be taken into consideration.

If, of n values, the difference of each individual value from the average value, *i.e.*, the error, is Δ, then the *mean error of a single measurement* is $\pm\sqrt{\frac{\Sigma\,\Delta^2}{n - 1}}$, and the *mean error of the result* is $\pm\sqrt{\frac{\Sigma\,\Delta^2}{n(n - 1)}}$. In the example already given the mean error of a single resistance measurement is

$$\pm\sqrt{\frac{1{\cdot}7^2 + 0{\cdot}5^2 + 1{\cdot}0^2 + 0{\cdot}2^2 + 1{\cdot}8^2}{4}}\,\Omega = 1{\cdot}4\,\Omega$$

i.e., 0·5 to 0·6 per cent. of the value; the mean error of the result is

$$\pm\sqrt{\frac{7\cdot 42}{20}}\,\Omega = 0\cdot 6\ \Omega = \tfrac{1}{4}\text{ per cent.}$$

It follows from the formula that if four times as many observations are taken (each of the same average accuracy), the error is reduced to one-half. If the mean error is multiplied by $\frac{2}{3}$, then the "**probable**" **error** is obtained (in the aforementioned example 0·9 Ω for a single reading, 0·4 Ω for the average). It can be asserted with equal probability that the result 250·3 Ω is about 0·4 Ω too high, or 0·4 Ω too low. The *weight* of a result is inversely proportional to the square of its mean error.

Interpolation.

If a certain magnitude has been measured under different conditions, *e.g.*, the density of a solution at different temperatures, or the difference of refractive index between water and solutions of different concentration, then the connection between the two variables can be shown graphically, or by means of a formula.

It is always advisable to make a graphic representation on squared paper, since it illustrates clearly the nature of the connection, and permits a convenient *interpolation*, *i.e.*, within the limits of observation, for any value of one variable the corresponding value of the other can be found. A continuation of the curve beyond the limits of observation—an *extrapolation*—always involves error. If in a particular experiment a smooth curve is drawn between the actual points observed, so that as many points lie above the curve as beneath it, and the sum of the negative deviations is approximately as great as that of the positive, then the observations have been "smoothed" at once in the most convenient way.

More exact, but more complicated than the graphic method, is the algebraical. If x and y are two variables, in certain cases a linear equation suffices to represent the relation between them:—

$$y = A \pm Bx;\ (\text{or } x = a \pm \beta\, y).$$

In most cases a parabolic equation must be used, of the form

$$y = A \pm Bx + Cx^2 \text{ (or } y = a \pm \beta\, x \pm \gamma\, x^2\text{)}.$$

Equations in x^3 and y^3 are seldom necessary. Values for the constants are easily obtained by combining the results of two or three observations. The agreement between formula and measurement can be improved by applying simple tests, *e.g.*, by changing the zero values A and a respectively. Or, making equal use of the data, several values for each constant are determined, as independent as possible of one another; their average value is taken, assuming an equal degree of accuracy for each of them. The most accurate method of correction is that of "least squares"; this can scarcely be employed with advantage in physical chemical exercises since the calculation is far too complicated, considering the relatively low degree of accuracy of the numbers obtained.

In the application of these methods also much time and unnecessary labour is saved by use of a previously arranged scheme of calculation. (For further details of these methods, and the mathematical interpretation of the experimental data, see Kohlrausch's *Lehrbuch der praktische Physik*, or Ostwald's *Physico-Chemical Measurements*.)

Accuracy.

Since the actual quantities measured are nearly always functions of more than one variable, it is necessary to scrutinise the influence of the different sources of error (preferably by taking logarithmic differences).* The best experimental arrangement, giving rise to the greatest accuracy, can often be seen from such a scrutiny (*e.g.*, use of the middle of the bridge-wire in measuring electrolytic

---

* Let x be the observed value, y that which is required. It is desired to find the relative change in y if the error of measurement of x is dx, and its relative error is accordingly $\frac{dx}{x}$. In other words, the relation between $\frac{dy}{y}$ and $\frac{dx}{x}$ must be found, *i.e.*, between $d \ln y$ and $d \ln x$.

Example.—The electrical resistance of a solution is measured by the Wheatstone-bridge method. Let this be y, let the circular bridge be conductivities (p. 134), and use of an angle of deflection of about 45° in the tangent galvanometer (p. 142)).

The error in the least accurately determinable variable is estimated from the probable error of reading, the probable error of the instrument, finally also from the influence of variations of temperature and pressure, etc. The errors in magnitudes which are easily ascertained (such as time, volume, weight, and length measurements) should be made so small that they do not count in comparison with the unavoidable error. *E.g.*, the weights of the dissolved substance, and of the solvent must be determined to within 0·2 per cent., if the unavoidable error in determining the depression of freezing point is 2 per cent.

Arithmetical calculations must always be made only so accurately that the last decimal is uncertain. Nothing is so unscientific as pretence at a pseudo-accuracy shown by many decimal places. On the other hand, it is necessary to take care that the experimental data are fully utilised. Every figure read must be noted. If a Beckmann thermometer has been read to about one-thousandth of a degree, and an actual reading is 1·320°, then the figure 1·32° is *incorrect*, because the hundredths of a degree can be read with certainty. The

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divided into ten parts (see p. 134), and the bridge-reading be x, the fixed resistance R. Then:

$$y = R\frac{x}{10 - x};\ \text{hence } \ln y = \ln R + \ln x - \ln(10 - x)$$

$$\frac{dy}{y} = \frac{dx}{x} + \frac{dx}{10 - x} = dx\left(\frac{1}{x} + \frac{1}{10 - x}\right) = 10\,\frac{dx}{x\,(10 - x)};$$

$\frac{dy}{y}$ will be very small when either dx becomes zero, or the denominator $x\,(10 - x)$ reaches its maximum value. The latter happens, as a second differentiation shows, when $x = 5$, *i.e*, when the middle of the wire is used. Accordingly $\frac{dy}{y} = 2\,\frac{dx}{x}$, *i.e.*, the relative error of the resistance determinations is twice as great as the error of the bridge-readings. If the bridge-reading be considered as free from error, but the corresponding resistance R as possibly incorrect (this is *not* the case in practice), it results directly that $\frac{dy}{y} = \frac{dR}{R}$. The error in the result is consequently directly proportional to that of the resistance.

In a similar way the determination of current strength by the tangent galvanometer (p. 141) and Kundt's method for the determination of c_p/c_v (p. 68) should be discussed.

reading 1·32 indicates, however, that either 1·31° or 1·33° might be considered correct. The correct reading, 1·320°, indicates that the thermometer stands between 1·319° and 1·321°.

Weighing.

The precautions necessary in carrying out exact weighings must be sought for in physical handbooks. The following general remarks may be permitted here :—

Apart from a few exceptions, a weight determination is so accurate in comparison with other measurements (of temperature, potential difference, length, etc.) that this accuracy cannot be completely utilised. For example, if the depression of the freezing point in a fourth-normal solution of a non-electrolyte is measured, the result under usual conditions is within one or two per cent. of the real value. It is therefore sufficient to know the weight of the dissolved substance and of the solution to within 0·1 to 0·2 per cent. If 25 to 30 grams of a fourth-normal cane-sugar solution is taken, the sugar need be weighed only to within 3 milligrams, and the water can be measured with a pipette, without paying attention to the difference between a cubic centimetre and a gram of water at room-temperature. In very many cases weighings can be carried out on a balance sensitive to 0·1 to 0·2 gram.

If, however, a really accurate weight has to be determined, to one-tenth of a milligram (*e.g.*, in the preparation of a dilute solution), trivial sources of error must be avoided. The vessel in which the substance is to be weighted should not have a needlessly large glass surface; differences of temperature must be avoided. It must be considered whether a reduction of the weights to a vacuum is necessary (the reduction for a substance of unit density amounts to more than 1 per cent.*). In addition, care must be taken in all cases that the substance is so definite, chemically, that it neither contains moisture, nor absorbs it, nor is otherwise impure.

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* In such a case one gram of substance displaces one cubic centimetre of air, while one gram of brass displaces only $\frac{1}{8\cdot4}$ = about 0·12 c.c. The difference, 0·88 c.c., weighs 1·06 milligrams, since the specific gravity of air at room temperature is 0·0012.

The zero of the balance must be determined before each weighing, unless the weight of a substance is found from the difference of two weighings made immediately the one after the other. All accurate measurements are made by the method of swings. The average of three or five swing-readings of the pointer on the scale of the balance is taken. The sensibility of the balance is found previously in terms of the same scale.

The Thermometer.

Numerous important physical-chemical magnitudes are affected greatly by change of temperature. Examples include the density of gases, solubilities, conductivities, refractive indices, rotation of light by solutions, and re-action velocities. Hence the determination of temperature plays an important part in other spheres as well as that of true thermo-chemistry. Mercury thermometers are usually employed.

When a result does not depend on a *difference of temperature*, but an absolute measurement, accurate to within 0·1°, is necessary, the thermometer must be standardised. This can be done either by carefully determining its zero-point, or by direct comparison with a standard thermometer at approximately the temperature at which the work is to be carried out. If the thermometer is not very old, or has been artificially *aged*, the blown-out glass (being a supercooled liquid) is still contracting slowly, and the zero-point alters with the alteration in volume. This constant slow contraction can be increased, but on the other hand, its effect can be masked completely by the phenomena of the *after-effect*. These are the results of rapid and strong heating and cooling; the former is more injurious, and is therefore to be considered more. The thermometer *recovers* slowly from the great expansion following on the violent application of heat, since the glass becomes brittle as it cools to room temperature, and offers more resistance to any change of form. The larger bulb-volume corresponding to the high temperature persists on rapid cooling, and the normal value is regained but slowly.

By infinitesimally slow cooling the after-effect can be avoided.*

On account of this after-effect, if a delicate thermometer has been used at high temperatures, before it can be used for a low temperature a zero-point determination is essential. Where differences of temperature are measured (*e.g.*, in calorimetric work, or determinations of rise of boiling points, or lowering of freezing point), since true temperatures need not be recorded, the principle of the after-effect does not apply, provided that during such measurements the thermometer is not removed from the solution or exposed to considerable changes of temperature.

It can be stated generally that the accuracy of no instrument is so often over-estimated as that of a mercury thermometer; further, in no other instrument are so many difficulties encountered where great accuracy is required. Under the most favourable conditions the maximum accuracy is only 0·1 to 0·2 per cent.

It is always advisable, in order to overcome the *sticktion* of the mercury thread in the capillary, to tap the *side* of the thermometer (tapping the upper end, as formerly recommended, is to be avoided). Measurements read with a slowly rising thermometer are more accurate than those when it is slowly falling.

Unless the whole of the mercury thread is heated equally with the bulb, a correction should be applied to the actual scale reading. In such cases as the Beckmann thermometer (p. 42), where a thread of mercury is outside the region of temperature measured, strictly speaking a correction ought always to be applied. All thermometers with variable range are calibrated at the ice-point. If a degrees of mercury are separated from the bulb of the thermometer, then it is easily seen that a degree has now the value $(1 + 0{\cdot}00016\, a)$ degrees, where 0·00016 is the *apparent* expansion-coefficient of mercury in glass. (The apparent expansion-coefficient is the difference between the cubical expansion-coefficient of mercury [0·000181] and that of glass [average value 0·000024].)

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* A familiar analogy to this after-effect of the velocity of cooling is the different hardness of steel when cooled slowly, or by quenching.

If a thread a degrees long, joined to the mercury in the bulb, differs on an average by dT from the actually measured temperature, the thread-correction is $a \times 0{\cdot}00016 \times dT$ where dT may be positive or negative.

This correction is generally most inconvenient and uncertain to estimate. A rough calculation, therefore, should be made in all cases to ascertain whether it lies within the error of experiment and can be neglected.

Where accuracy is desirable, constant stirring is necessary, so that the thermometer registers the true mean temperature of the gas or liquid in which it is placed. This stirring must be the more regular and rapid the smaller the temperature-difference to be measured, and the larger the space concerned. On the other hand, it must not be so vigorous that the heat of stirring becomes perceptible; this can be easily tested by a blank experiment carried out under similar conditions.

(With regard to the calibration of a thermometer, larger text-books must be consulted.)

The Barometer.

Only mercury barometers, and where possible the siphon form of instrument with upper and lower tubes of equal width, are permissible for exact measurements. With such an instrument, as the difference in height between two equal meniscuses is measured, a correction for capillarity is avoided. Before taking a reading, both surfaces are shaken by gentle side-taps. The barometric height is always reduced to zero temperature, *i.e.*, the length of the column of mercury at room-temperature is corrected to that which it would measure at 0°. The correction $\frac{t}{8}$ mm. can be applied as a first approximation, where t is the temperature of the mercury.* Under normal conditions the correction amounts to 2 or 3 mm., which is $\frac{1}{4}$

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* The length of the mercury column is, on an average, 750 mm. = $\frac{3000}{4}$ mm.; the cubical expansion coefficient of mercury, minus the linear expansion coefficient of the scale (brass or glass) is 0·00016 to 0·00017, *i.e.*, about 1/6000. Replacing $\frac{750}{1 + 0{\cdot}00017\,t}$ (see p. 2) by $750 - 750 \times 0{\cdot}00017\,t$, the correction to be subtracted is $\frac{3000\,t}{4 \times 6000} = \frac{t}{8}$ mm.

to $\frac{1}{3}$ per cent. of the observed value, and in all gas measurements it is applied directly in the calculation. Exact corrections are given in Table III.

While in most cases all lengths are given in centimetres, in barometric and all other pressure measurements it has become customary to express the results either in *atmospheres* or in millimetres.

Washing and Drying Glass Apparatus.

Rinsing with tap-water, and once with distilled water, is always sufficient except for conductivity measurements. Drying with ether should be avoided since it always leaves a residue. Alcohol is used for vessels which cannot be strongly heated. The most convenient method is to suck or blow dry air through the vessel, which is heated at the same time. Where, as with thick-walled flasks, direct heating with a burner is not permissible, the vessel is steamed out until the walls no longer show drops of water,—for this purpose water is heated in a thin metal can, such as is used in distillation with steam, closed with a cork through which passes a glass tube, conducting the steam to the vessel under treatment—the flask is then wrapped in a cloth, and air blown through by means of blowpipe bellows, until the last traces of moisture have evaporated. The method is especially advisable when several vessels in succession have to be dried. When the steaming is continued for a considerable time, it dissolves most of the soluble substances, especially alkalies, from the glass surface (see p. 133).

Conclusion.—*The student must accustom himself to make a* **very careful record** *of his work*, **to make a rough diagram** *of the experimental apparatus*, **to note distinctly the whole of the observations**, *and to separate carefully observation and calculation. Where the results show large divergences from the correct value* (which, e.g., can be found in **Landolt-Börnstein**) *their source must be traced by considering the conditions of experiment, and of measurement, in order to detect the probable uncertainty.*

Where a chemical reaction is studied, its equation must be *given—with electrolytes the Ionic equation—and the significance carefully considered.**

No constants may be employed unless their significance and origin are taken into account.

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* For example, consideration of an equation representing neutralisation shows that, if strong acids and alkalies are used, only the heat of dissociation of water is measured. The equation

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = H_2O + Na^{\cdot} + Cl' + q \text{ cal.}$$

is essentially

$$H^{\cdot} + OH' = H_2O + q \text{ cal.}$$

CHAPTER II

THE DETERMINATION OF DENSITY

The Gas Law ($PV = RT$).

The fundamental law of that part of Physical Chemistry which relates to gases and dissolved substances is a combination of

1. the **Boyle-Mariotte Law**: $pv = p_0 v_0$;

2. the **Gay-Lussac Law**: $p = p_0 (1 + \frac{1}{273} t)$,

$$v = v_0 (1 + \frac{1}{273} t),$$

which is the basis of our definition of temperature;

3. **Avogadro's hypothesis**, that, under the same conditions of temperature and pressure, equal numbers of molecules occupy equal volumes.

All three laws are limit-laws, *i.e.*, they are only true within limits, namely, for very low pressures and at high temperatures.*

The **gram-molecule** is chosen as unit of mass; the mass and volume connected by this unit are denoted by P and V respectively. Thus let a gram-molecule of gas at pressure P_1 occupy the volume V_1, or if compressed to volume V_1 let it exert a pressure P_1. To pressure P_0 corresponds volume V_0, and to pressure P, the volume V. Substituting P and V in equations 1 and 2, by a slight transformation we obtain the expression—

$$PV = \frac{P_0 V_0}{273} \cdot (t + 273).$$

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* Strictly speaking, this also is incorrect, for could exact measurements be made under these conditions they would show perceptible dissociation; part of the molecules would have split up into atoms.

It follows from equation 3 that the term $\frac{P_0 V_0}{273}$ possesses the same magnitude for all gases; this universally applicable constant is named R, *the gas constant.*

If we reckon from $-273°$,* instead of from 0°, then temperatures are expressed in the *absolute* scale ($T = t + 273°$). The gas-equation then reduces to the simple form :

$$P V = R T.$$

The Gas-constant R.

This expression, when multiplied by T, obviously has the dimension of a work ($pv = l^{-1} mt^{-2} l^3 = l^2 mt^{-2}$); it can be expressed in absolute units (cm. g. sec), in terms of mass and heat (g-cal), or in other units. The numerical value is determined in the following manner :— †

The basis of all molecular weights is 32·00, that of a molecule of oxygen ; 32 grams of oxygen occupy at 0° and 760 mm. pressure, *the normal conditions of temperature and pressure* (*N. T. P.*), a volume of 22390 c.c. (V_0), since 1 c.c. O_2 weighs under these conditions 0·0014294 g. Usually the figure for V_0 is taken as 22410 c.c. ($2·41 \times 10^3$ cm^3), the average of the molecular volumes of H_2, N_2, and O_2, which are not absolutely equal since the laws are not absolutely true (but limit-laws).

The pressure of one atmosphere (P_0) is in absolute units $76 \times 13·596 \times 980·6 = 1013200 \frac{\text{Dyne}}{\text{cm}^2} = 10·132 \times 10^5$ Dyne cm^{-2}. Consequently, in absolute units,

$$R = \frac{22·41 \times 10·132 \times 10^8}{273}$$

$= 0·8317 \times 10^8$ Dyne cm. $T^{-1} = 0·8317 \times 10^8$ Erg. T^{-1}. In order to convert R into heat units, this value must be divided by the mechanical equivalent of heat (of a calorie at

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* At the temperature $-273°$ all gases, theoretically, occupy zero volume.

† For more exact details (comparison and discussion) see D. Berthelot, *Zeitschr. f. Elektroch.* 10, p. 621, 1904, and Nernst, *ibid.*, pp. 629 and 882.

15°) 0·419 × 10^8: the result is **1·985 cal.** T^{-1}, which can be taken as approximately 2 cal. In *litre-atmospheres*

$$R = \frac{22{\cdot}41}{273} = 0{\cdot}0821.$$

For its value in electrical units see p. 112.

A complete comparison of the most important physical-chemical constants is given in Table I.

Reduction of the Volume of a Gas to Normal Temperature and Pressure.

If the volume of a gas (v) is measured while it is under a pressure p and temperature t*, then at 0° and 760 mm. pressure the volume will be:—

$$v_0 = \frac{v \times 273 \times p}{(273 + t)\,760} = \frac{v \times p}{273 + t} \times 0{\cdot}3592.$$

This can be written approximately

$$v_0 = \frac{v \times p \times 0{\cdot}36}{273 + t}.\dagger$$

If a gas has been collected over a liquid which has an appreciable vapour-pressure, such as water, then a correction must be made for the amount of vapour in the gas volume. For this purpose application is made of **Dalton's law**, that the pressure of a gas mixture is equal to the sum of the pressures which each individual gas would exert if it alone occupied the space. Therefore, if the water-vapour tension at temperature t is w_t (see Table II.) and the total pressure is p, then the partial pressure of the gas which is being measured is $p - w_t$, and the reduction formula takes the form

$$v_0 = 0{\cdot}3592 \frac{v\,(p - w_t)}{273 + t}.$$

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* To determine exactly the temperature of the gas the eudiometer or gas burette which contains it is fitted with a water jacket, and the temperature of the water observed.

† If an accuracy greater than one per cent. is not desired, the following rough corrections can be used: For every $\frac{3}{4}$ mm. that the pressure is above or below 760 mm. of mercury, add or subtract 0·1 per cent. of the volume; similarly for t = 19°, subtract 1/15th of the volume. If the temperature is not far removed from 19°, a correction is first made to that temperature by assuming that the expansion-coefficient of the dry gas is 1/300th per degree; thereafter the previous correction to 0° is made.

Exercises.

On equation 1 : $pv =$ const.

A long eudiometer is taken, and half filled, first with air, and then with hydrogen, over mercury. In each case the pressure and volume are altered by raising and lowering the eudiometer (see Fig. 1), and a series of products, pv, is obtained for both gases. In order to prevent transference of heat from the hand, a thick cork is pushed over the end of the eudiometer (see Figure). With a Hempel gas-burette of 100 c.c. capacity the law can be proved easily by subtracting the observed heights from the atmospheric pressure, remembering that a column of water 1 cm. high corresponds to one of mercury $\frac{3}{4}$ mm. high.

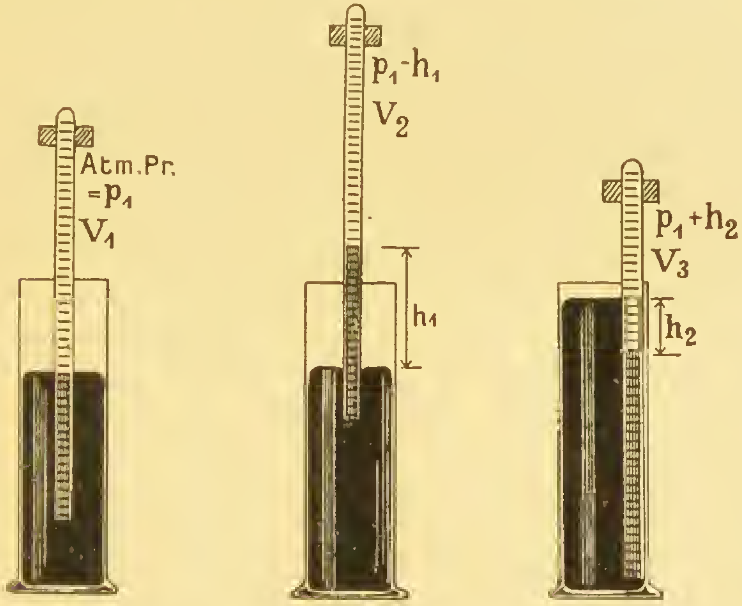

FIG. 1.

On equation 2 : $v = v_0 (1 + \frac{1}{273} t)$.

An amount of air, which would measure at 0° and a pressure of one atmosphere 273 c.c., is confined in a flask. In order to effect this a flask of capacity about 300 c.c., with bored rubber stopper, is weighed, filled with water, and again weighed (let this amount of water be J c.c.). After drying (J − 273) 13·6 g. of mercury are poured in. The mouth of the flask is closed by a cork containing a narrow bent leading tube (see Fig. 2). The flask is surrounded by ice until the gas is cooled to 0°. The gas which escapes on warming the flask first to room temperature t and then to 100° respectively is collected in a eudiometer, over water; when reduced to N. T. P. it measures t c.c. and 100 c.c. respectively. The experiment should be repeated with hydrogen.

On the third law: the equivalence of molecular volumes of gases under similar conditions.

One gram of marble (equal to 1/100th of a gram-molecule of $CaCO_3$) is dissolved in dilute HCl, and the gas evolved collected over a saturated solution of NaCl (water would dissolve too much gas). An exactly similar experiment is made with 0·65 g. zinc (which is 1/100th of a gram-molecule of zinc relative to hydrogen). It will be found that the two volumes are nearly equal, corresponding to about 220 c.c. at N. T. P.

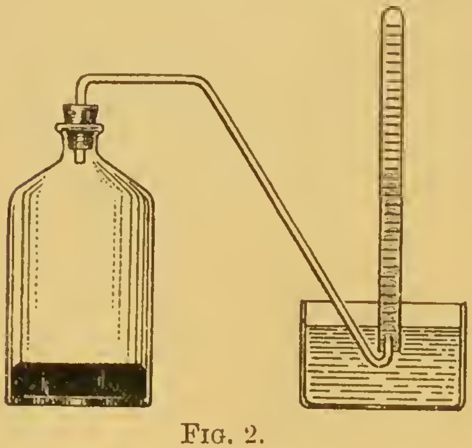

FIG. 2.

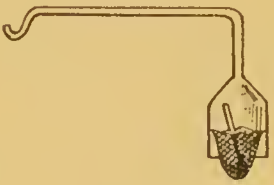

FIG. 3.

Bent glass funnels of the form shown in Fig. 3 serve for the introduction of the solids into a glass beaker filled with the dilute acid; these solids are enclosed in a piece of copper wire-gauze.

Density. Specific Gravity.

The density of a substance is the mass of unit volume; it is accordingly a number of the dimension ($l^{-3}\ m$). The specific gravity of a substance is the ratio of its mass (or its weight in a vacuum) to the mass (or the weight) of an equal volume of water at 4° (also corrected to a vacuum), therefore the specific gravity is only a ratio. The terminology does not distinguish with sufficient accuracy between the two definitions; and the shorter term *density* is also usually used merely as a dimension number.

The standard units, exclusively used in scientific work, are: for specific gravity, water at 4° corrected to vacuo (sp. gr. = 1), and for unit of volume, the real cubic centimetre, exactly defined by the normal metre in Paris. The so-called Mohr's value for the cubic centimetre, with which most of the older flasks, pipettes, and burettes are graduated, is about $\frac{1}{4}$ per cent. too great, since it represents the volume of 1 gram of water at room temperature, weighed with brass weights, and not corrected to a vacuum. It is necessary to apply a correction when such vessels are used for exact density determinations in cases such as the preparation of standard solutions.

The extreme specific gravities which are as yet known (hydrogen at N. T. P. and osmium) are in the ratio 1 : 250,000. In spite of this great range, nearly all are estimated by similar methods—weight and volume determinations—although the instruments employed vary with the nature of the substance.*

Specific Gravity of Gases. Methods depending on Weight.

The chief difficulty in weighing a gas lies in its very small specific gravity. The error due to the air displaced is frequently greater than the weight to be determined.

In order to be independent of slight variations in the density of the air, and at the same time to eliminate error arising from the large area of the containing vessel, a closed flask of almost equal capacity, weight, and area is chosen as counterpoise. The vessel in which the gas is to be weighed (a small glass bulb) has two small well-ground glass taps †; the volume of the bore of the taps must be added to that of the bulb. To determine this total volume, the bulb is first weighed, either evacuated, if the walls are sufficiently strong (weight found, m_0), or filled with air of density σ, at pressure p, and temperature t (weight m). It is then filled with a liquid of known specific gravity, and again weighed (water or mercury, specific gravity S, weight M). If the vessel is filled with mercury, this can be displaced directly by the gas ; similarly, when the bulb is exhausted, the method of filling with gas is obvious. If, however, the bulb contains air, the gas to be experimented with must be led through for a long time in order to displace the air completely ; the gas escaping through the second tap should be tested, if possible, by some chemical method, as, for example, absorption, to show that the displacement is complete. The bulb is then weighed, and its pressure and temperature noted ; let these be respectively m_1, p_1, and t_1.

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* The only important method depending on another principle is Bunsen's diffusion method.

† The taps should be well greased ; the lubricant used by Ramsay is extremely good. It is prepared by warming together until they melt one part of paraffin, three of vaseline, and six of soft rubber.

It is customary in expressing the specific gravity of gases to take as unity dry air,* free from carbon dioxide, and at the same pressure and temperature (this gives the vapour or gas density).

To derive the molecular weight of a gas from its known density, this must be multiplied by the mean molecular weight of air (28·9 if $O_2 = 32$); the true specific gravity, compared with water at 4°, is found by multiplying the density relative to air by 0·001293, the specific gravity of dry air at 0° and 760 mm. pressure.

Formulæ for gas density,

(*a*) when the bulb has been evacuated—

$$\sigma_1 = \frac{(m_1 - m_0)\,S}{(M - m_0)\,\sigma} \qquad \sigma = \frac{0{\cdot}001293 \times 273 \times p_1}{(273 + t_1)\,760}$$

$$\frac{760}{0{\cdot}001293 \times 273} = 2153$$

$$\sigma_1 = \frac{(\mathbf{m}_1 - \mathbf{m}_0)\,\mathbf{S}\,(273 + \mathbf{t}_1)}{(\mathbf{M} - \mathbf{m}_0)\,\mathbf{p}_1} \times 2153.$$

(*b*) when the bulb has been weighed full of air—

1. Let the pressure and temperature of the *dry* air and the gas be p and t respectively (the barometric pressure and temperature in the balance room).

$$\sigma_1 = \frac{(m_1 - m)\,S}{(M - m)\,\sigma} + 1.$$

Proof.—Let L be the true weight of the air-content, G that of the gas-content, then—

$$G - L = m_1 - m\,;\ G = m_1 - m + L\,;\ L = \frac{(M - m)\,\sigma}{S}$$

$$\sigma_1 = \frac{G}{L} = \frac{m_1 - m}{L} + 1 = \frac{(m_1 - m)\,S}{(M - m)\,\sigma} + 1\,;$$

σ is as above— $\dfrac{p}{(273 + t)\,2153}$

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* Damp air is lighter, for the molecular weight of steam is about 18, the mean molecular weight of air about 29, a ratio of 0·62 to 1. Hence, if the vapour pressure of steam is w, the atmospheric pressure p, then the density of dry to damp air is in the ratio $p : (p - 0{\cdot}38\,w)$. The tension of water vapour is in ordinary room air about 50 per cent. of the maximum amount; at temperature t (15—22°) the maximum tension w is roughly equal to $0{\cdot}87\,t$ (cp. Table II.). As a first approximation for p, we can substitute the expression $p - 0{\cdot}5 \times 0{\cdot}38 \times 0{\cdot}87\,t = p - \frac{t}{6}$.

Hence $$\sigma_1 = \frac{(m_1 - m)\,S\,(273 + t)}{(M - m)\,p}\,2153 + 1.$$

2. Let the pressure and temperature of the gas be p_1 and t_1, and of the air used (*damp*) be p and t (the barometric pressure and temperature in the balance room); it follows that—

$$\sigma_1 = \left(\frac{(m_1 - m)\,S}{(M - m)\,\sigma} + 1\right) \cdot \frac{\left(p - \frac{t}{6}\right)}{p_1} \cdot \frac{(273 + t_1)}{(273 + t)};$$

but $$\sigma = \frac{0{\cdot}001293 \times 273\left(p - \frac{t}{6}\right)}{(273 + t)\,760} = \frac{p - \frac{t}{6}}{(273 + t)\,2153};$$

Hence,—

$$\sigma_1 = \left(\frac{(m_1 - m)\,S\,(273 + t)\,2153}{(M - m)\left(p - \frac{t}{6}\right)} + 1\right)\frac{\left(p - \frac{t}{6}\right)}{p_1} \cdot \frac{(273 + t_1)}{(273 + t)}.$$

Remark.—It has been taken for granted that in formula (*b*) the air displacement of the bulb is taken into consideration only when weighing the gas, not when weighing with water or mercury. In the last case the displacement is always neglible, since the brass weight displaces about as much air as the mercury. The weight of water $(M - m)$ can be corrected for displacement by multiplying by 1·001.

Experiment.—Determine the densities of carbon dioxide and coal-gas by means of a small bulb of from 100—150 c.c. capacity. The weight of the bulb when evacuated or filled with gas must be determined with the greatest possible accuracy. An ordinary balance can be used when weighing water; if possible, the bulb should be weighed both evacuated and filled with air, and the measurements controlled by this actual determination of air density.

Determination of Gas Density by Diffusion Measurements.

Bunsen devised a method for the determination of gas densities which obviates the necessity of weighing. If equal volumes of two gases, whose specific gravities are respectively σ and σ_1, diffuse under the same pressure through the same tiny hole, then their specific gravities are approximately in the inverse ratio of the squares of the diffusion velocities; they are therefore directly proportional to the squares of the times of diffusion.

Proof.—If the gas diffuse from a space over mercury, so that M grams of mercury rise through h cms., while at one time m grams of one gas diffuse with velocity v, and at another time, m_1 grams of a second gas with velocity v_1, then

$$Mgh = \frac{mv^2}{2} \text{ and } Mgh = \frac{m_1 v_1^2}{2};$$

hence, $\frac{v^2}{v_1^2} = \frac{m_1}{m} = \frac{\sigma_1}{\sigma}$, or if the times of diffusion are τ and τ_1:

$$\frac{\sigma_1}{\sigma} = \frac{\tau_1^2}{\tau^2}; \quad \sigma_1 = \sigma \frac{\tau_1^2}{\tau^2}.$$

In this simple calculation no account is taken of some disturbing phenomena which take place at the small hole. The gas does not pass through in a regular current, but vortices occur; these need not be taken into consideration here.

The apparatus is standardised with a gas of known density. It consists of a glass tube ending in a two-way stop cock (see Fig. 4). The direct opening is closed by a piece of tinfoil or platinum foil containing a very small hole, and cemented to the glass; the opening through the tap is used to fill the apparatus with gas. The tube stands in a glass jar containing mercury, and is always immersed to a certain definite point. Inside the tube the mercury supports a glass float, on which are etched two marks. When the tap is turned to communicate with the tinfoil, the time which elapses between the two moments when the upper and lower marks pass the cross thread of an ordinary telescope is found by means of a stop-watch. The method is not very exact, and requires rather a large quantity of gas.

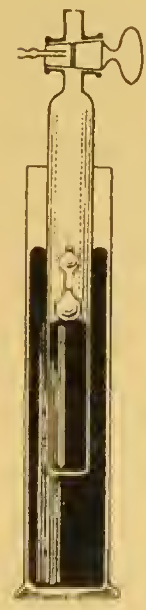

FIG. 4.

Experiment.—Standardise the apparatus with air and then determine the densities of carbon dioxide and coal-gas.

Determination of Vapour Density.

Gases which condense to liquids at pressures not much above atmospheric pressure are called *vapours*. They obey the gas laws less accurately than ordinary gases. *Vapour densities*, as distinguished from gas densities, refer to those substances which have been weighed in solid or liquid form. Vapour density determinations have become of great importance to the chemist, since they show either the molecular weight of a substance, or if that is known, the degree of dissociation. As in the previous method of measurement, the density of air under the particular conditions of experiment is chosen as unity. It is more rational, where possible, to determine the molecular weight directly.

Vapour densities can be measured in one of three ways :—(*a*) A solid or liquid is first weighed, and then the volume which it occupies as gas is found (method of Hofmann and Viktor Meyer); (*b*) a given volume of steam or vapour is weighed (Dumas' method); (*c*) the increase of pressure which a known weight of solid or liquid produces when evaporated at constant volume, is measured.

The last is the most complicated, so that what in principle is an elegant method is but little utilised. Hofmann's method is almost entirely supplanted by the less exact but more convenient and elegant method of Viktor Meyer.

Determination of Vapour Density by Viktor Meyer's Method.

A known quantity of liquid is vaporised rapidly in an enclosed space filled with air, which is at the same temperature as its surroundings; the vapour produced drives out an equal volume of air, which is caught in a eudiometer over water and is measured at room temperature. The temperature at which the liquid vaporises need not in consequence be known. Moreover, for the same reason, the space in which evaporation takes place need not be at the same temperature throughout; it need only possess stationary conditions, as set up by radiation from a heat jacket, in which the air-space receives as much heat from the boiling liquid as it loses by radiation. If the evaporation takes any appreciable time, the vapour may diffuse into the upper part of the tube, or even into the exit tube and eudiometer, and condensing, introduce error into the volume determination. The danger of diffusion is greater the higher the temperature, and the evaporation must therefore be completed as quickly as possible. With substances which need not be raised to a high temperature, and which do not react with it, the addition of a little mercury, an excellent conductor of heat, to the bulb *D*, where evaporation takes place, is useful (see Fig. 5). *A* is a simple release contrivance, by which the small bottle *B* is allowed to fall as soon as the temperature becomes constant; this is shown when no more gas bubbles escape from *C*, when the graduated eudiometer previously filled with water is placed over the opening. *B* contains the weighed substance and has a ground-in stopper. The releasement is brought about simply, by drawing out the glass rod held in position by the rubber tube, until *B* falls. The gas collected in the eudiometer is measured. At the end of every experiment the vapour is blown out of the evaporation bulb; this must always be kept perfectly dry.

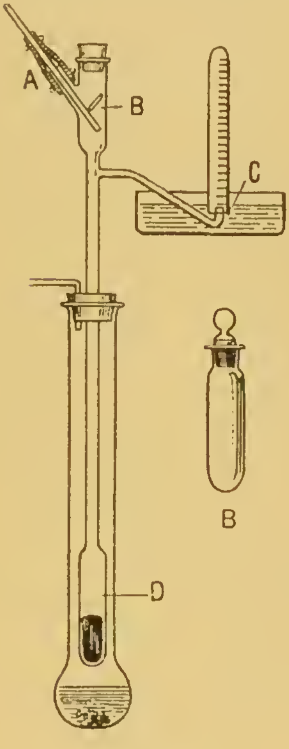

FIG. 5.

Let *a* mg. be the weight of substance, and *v* c.c. (about 40—50) the volume of air measured, at t° and *p* mm. pressure (when the water stands higher inside than outside the eudiometer, the difference of level, expressed in height of mercury, is subtracted from the pressure). Let w^t be the vapour pressure of water at t° (see Table II.). Then, since a milligram-molecule of gas at N. T. P. occupies 22·4 c.c., the molecular weight *M* is obtained directly from the equation—

$$\frac{M}{a} = \frac{22{\cdot}41}{v_0} = \frac{22{\cdot}41 \times a\,(273 + t)\,760}{v\,(p - w_t)\,273} = 62{\cdot}38\,\frac{a\,(273 + t)}{v\,(p - w_t)}.$$

Before the flame is removed from beneath the boiling tube, the cork at the top of the apparatus must be loosened.

The method is applicable for any temperature; it follows from the description which has been given that the only difficulties which can arise at very high temperatures are connected with the material of the vessel, and the very small air displacement of the substance itself (cp. Nernst, *Zeitschr. f. Elektroch*, 9. 622, 1903). The vapour densities of dissociating substances are dealt with on p. 27.

Exercise.—Determine the vapour density of chloroform or benzene at 100°.

Determination of Vapour Density by Dumas' Method.

The principle is the same as that used in the measurement of gas densities. A glass bulb, drawn off to a narrow capillary, is weighed, full of air, full of vapour, and finally full of water; (the volume of the bulb should be about 200 c.c.). After what has been said previously it is obvious that the first two weighings must both be carried out quite accurately on a very sensitive balance, though the water may be weighed with sufficient accuracy on a rougher balance.

To cause liquid to enter the bulb, the end of the capillary is dipped into a small glass beaker containing the liquid; the bulb is then warmed with the hand, so that bubbles of air escape; in cooling, a corresponding volume of liquid is sucked up into the bulb. It is then placed in a constant temperature bath, at least 10° higher than the boiling point of the liquid; in most cases a bath of boiling water suffices. Care must be taken that only the capillary projects outside the bath. The bulb is fastened in a wire stand or else the capillary is clamped by means of a cork in a hole in the roof of the water bath. The violently boiling liquid expels the air; when evaporation is complete, the capillary is warmed slightly to prevent the liquid condensing there, and the tip is sealed off with a mouth blowpipe. This can be done most easily by drawing off a very short piece of the capillary; the piece drawn off must be weighed with the bulb. As the liquid condenses, a partial vacuum is produced in the bulb; if it is inverted the capillary partly fills with the liquid. If it is not completely closed, a regular stream of small pearl-like air bubbles will be seen rising through the liquid, a sign that the experiment is unsuccessful and must be repeated. If a good seal has been made, the bulb, filled with vapour and a small quantity of liquid, is weighed, after carefully cleaning the surface. Then the end of the capillary is scratched with a short file or glass knife, and broken off under water. If all the air had been driven out of the bulb, it completely fills with water (if boiled out water containing no dissolved air is used ; otherwise some air escapes into the partial vacuum). In most cases some of the condensed liquid remains in the bulb. It is apparent that no appreciable error is introduced if a small quantity of water (a fraction of a gram) is replaced by a liquid of a different specific gravity. Expansion of the glass when warmed to the temperature of the bath leads to a somewhat larger error. If the bulb was filled with water at temperature t, and with vapour at temperature t_1, then the volume of the bulb has increased by $V \times 0{\cdot}000025\ (t_1 - t)$. In an experiment where $t_1 = 100°$, $t = 20°$, this amounts to $\frac{1}{5}$ per cent. It is taken for granted that the weight of water has been reduced to vacuo, a correction which amounts to about 0·1 per cent. in the same direction as that due to the alteration in volume of the glass vessel.

Formula : without the last correction :—

Weight of air m, temperature t, pressure p.
,, vapour m_1, ,, t_1, ,, p_1.
,, water M, specific gravity S.

$$\sigma_1 = \left(\frac{(m_1 - m)\, S\, (273 + t)}{(M - m)\left(p - \frac{t}{6}\right)}\, 2153 + 1 \right) \frac{\left(p - \frac{t}{6}\right)(273 + t_1)}{p_1\,(273 + t)}\ ;$$

(cp. pp. 20, 21).

S can be usually taken as equal to unity (Table II.); applying the corrections above-mentioned :—

$$\sigma_1 = \left(\frac{(m_1 - m)\, S\, (273 + t)}{(M - m)\, 1{\cdot}001 \left(p - \frac{t}{6}\right)}\, 2\,153 + 1 \right) (1 - 0{\cdot}000025\, (t_1 - t)$$

$$\times \quad \frac{\left(p - \frac{t}{6}\right)(273 + t_1)}{p_1\,(273 + t)}$$

$$= \left(\frac{(m_1 - m)\, S\, (273 + t)}{(M - m)\left(p - \frac{t}{6}\right)}\, 2153 + 1 \right)\left(1 - \frac{t_1 - t}{40000}\right)$$

$$\times \quad \frac{\left(p - \frac{t}{6}\right)(273 + t_1).}{p_1\,(273 + t)}$$

Exercise.—Determine the vapour density and molecular weight of chloroform or benzene.

The Dumas method is also practicable at all temperatures at which the material of the bulb is sufficiently capable of resistance. However, as the temperature rises the expansion of the vessel becomes an ever-increasing factor, whereas this leads to no error in the Viktor Meyer method. If substances are used which have no noticeable vapour pressure at ordinary temperatures, it is unnecessary to seal the vessel; by quickly cooling, *e.g.*, by immersing the bulb in *cold* water, the vapour condenses inside the bulb and air enters. By this means both experiments and formulæ are simplified. At high temperatures only a very small amount of substance can be taken, and this must be weighed with especial accuracy.

Vapour Density of Dissociating Substances.

At high temperatures and low pressures most molecules dissociate into smaller ones or even into atoms. Substances which are dissociated appreciably at temperatures easily attained are PCl_5, PBr_5, N_2O_4, NH_4Cl. These examples all belong to the same type of dissociation; from one molecule arise two, and the volume becomes doubled. If complete dissociation takes place, then a density determination gives the half molecular weight. If the theoretical molecular weight is M, and that found by experiment M_1, it is easily seen that $(\frac{M}{M_1} - 1) \times 100$ per cent. of the molecules are dissociated.

The degree of dissociation depends very largely on the pressure and temperature. Since during dissociation the volume increases, the degree of dissociation rises with decrease of pressure, because in a variable complex, when the pressure falls, the system occupying the larger volume is formed in preference to the other (Le Chatelier's principle of least resistance). By pressure is here understood the sum of the partial pressures of the undissociated gas and the products of dissociation. Now the partial pressure of the substance vaporised in the Dumas and Viktor Meyer vessels is different. The former contains only the vapour of the substance, hence its partial pressure is the whole pressure, and this is equal to the atmospheric pressure at the time of experiment. In the Viktor Meyer apparatus, however, the partial pressure varies throughout, from the bottom, where but little air is mixed with vapour, to the exit tube, where there should be nothing but pure air. The range varies from a pressure almost equal to atmospheric to zero; hence the molecular weight of dissociating substances, determined by this method, depends entirely on the velocity of evaporation and diffusion, the shape and size of the vessel, and in short is quite an indefinite value, but is always smaller than the well-defined value found by the Dumas method.

The Specific Gravity of Liquids.

The specific gravity is the most important constant of a liquid, whether for its characterisation and identification, for the analytical examination of solutions and mixtures, or as the chief factor in the determination of optical constants.

The weight and volume of liquids can be measured with equal accuracy; both are of the same order of magnitude, because that liquid with which comparison of weight and volume is made (water at 4°) is a liquid of *average* density. If mercury, which has the exceptionally high density of 13·6, is excepted, the densities of liquids in general use lie between 0·7 and 2. Weight and volume can be measured without difficulty with an accuracy of one part in 10,000, when moderate quantities of substance are used (about 10—20 grams or c.c.). Consequently the slide-rule, or 4-place logarithm tables, are *not* sufficient for such calculations. If an accuracy of more than 1:1000 is desired, all weighings must be corrected to vacuo.

According to the accuracy desired, the customary apparatus for density determinations becomes arranged in the following order: aræometer (hydrometer), 1 c.c. pipette, burette, Mohr's balance, larger pipette (10—25 c.c.), density flask, pyknometer.

The aræometer, or common hydrometer, is moderately accurate, when—as for many special purposes*—the body of the hydrometer is made very large and the neck very thin. In this case, for a small decrease in specific gravity, and therefore in the upward force exerted by the liquid, the instrument sinks through a number of scale divisions.

Ordinary hydrometers are accurate to about $\frac{1}{2}$ per cent.; this accuracy may be even less if the instrument does not float vertically, or is not well moistened at the surface between air and water. The latter cause of error is easily recognised by the accompanying irregularity of meniscus.

The **1 c.c. pipette** proposed by Ostwald allows an accuracy of one part in a thousand. The instrument can be easily made by the student, and, by weighing it empty and dry, and then filled to the mark with water or mercury, from the difference between the weights its capacity can be determined. The tube must be graduated for *filling*, not for emptying. The opening at the lower end is made so small that there is no leakage when the pipette is placed horizontally. The pipette is made so short that by means of a trestle of stout wire it can be placed horizontally on the pan of the balance. The weight of the dried pipette and stand is observed once and for all, or the wire stand is counterpoised with an accurate tare. If the pipette has been weighed full of water, and if it is used only for the determination of densities in the neighbourhood of 1, no reduction to vacuo is necessary, since the corrections for both weighings are equal within the limit of error. If the pipette has been calibrated with mercury, the calibration correction is negligible; if the densities to be determined are in the neighbourhood of 1, then 1 per thousand is added to the found density as correction.

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* *E.g.*, in the investigation of sea water, where it is desirable to determine rapidly small divergences from the normal value.

When a **burette** is used for density determinations, it is necessary to ascertain previously whether it is calibrated in Mohr's units or in true c.c. Errors from *parallax* in making readings, and from liquid sticking to the walls of the burette, must be avoided, the latter by making the outflow very slow.

Mohr's Balance is more elegant than either of the methods so far discussed. A glass float (frequently a small, thick thermometer) is suspended by a platinum wire from the end of one beam of a balance (divided into ten parts), and is balanced in air by means of a fixed weight on the second shorter beam. By means of a screw S the balance is adjusted so that the small point K at the end of the shorter beam is opposite the fixed point J. If the float is immersed in a liquid, on account of the upward force exerted by this, the equilibrium is disturbed, and the balance no longer remains opposite the zero point. Rider weights are supplied with the balance (see Fig. 6), of which the largest, A_1, suspended at the end of the

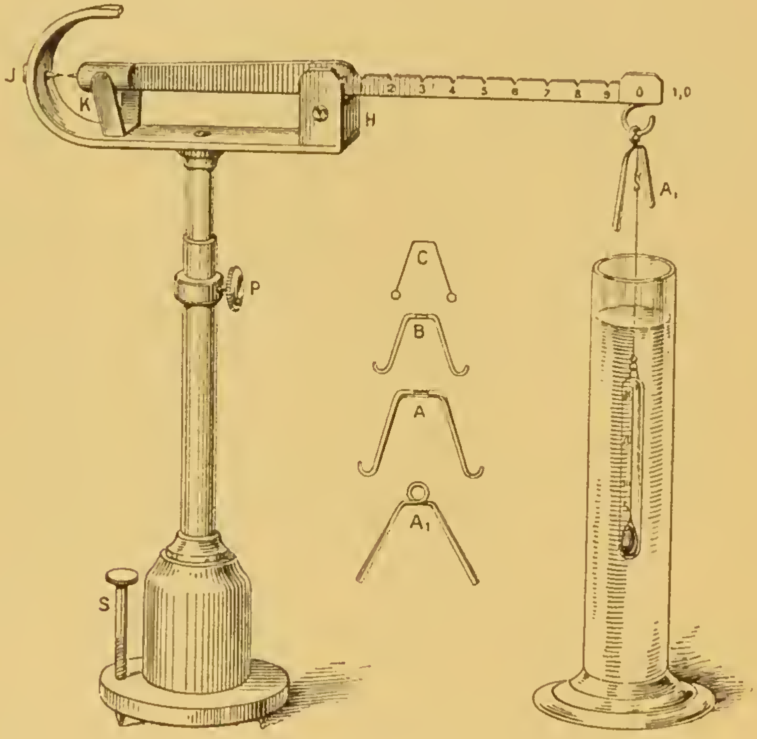

Fig. 6.

longer beam (at division 10) exactly compensates the displacement of the float in water at 4° C.

The smaller weights are $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$ of this unit. If the float is suspended in a liquid of specific gravity 1·035, then the upward force of the liquid is compensated when the unit weight is at the scale division 10, the tenth-weight at division 3, and the hundredth at division 5. It is necessary to take care that the float hangs freely in the liquid, that the wire is clean, and only a small part of it is submerged, so that a definite meniscus is formed. The balance is tested by means of a liquid of known specific gravity. If the accuracy of the riders is suspected, their relation to one another should be examined on an ordinary accurate balance. The error of a good Mohr's balance is about 0·0005. No correction need be applied at ordinary temperatures, although, strictly speaking, the volume and the corresponding displacement of the float depend on temperature; (change per degree 0·000025, the cubical expansion coefficient of glass).

The following remarks apply to the use of pipettes for density estimations. In determining the weight of the pipette filled with water and with liquid certain rules must be observed strictly. The liquid must not be blown out of the pipette; after the jet of water has run out, the pipette must be held vertically for half a minute, the lower end against the wet side of the receiving vessel, the upper opening closed. The pipette must always be rinsed with distilled water after use, and whilst not in use must be placed in a glass jar, with the smaller end upwards and covered by a small glass cap, to prevent the entry of dust.

Only *aqueous* solutions of not too great concentration can be measured accurately by means of pipettes. With concentrated solutions, and with organic liquids especially, the often considerable difference in viscosity may occasion a large error.

If burettes or pipettes do not appear to discharge their contents uniformly, the cause, traces of grease, must be removed by chromic acid mixture, which is allowed to stand in the vessels for a considerable time. In the case of tap burettes, the grease in the taps due to the grinding must be removed previously, and a small glass vessel placed beneath the tap. The bichromate solution and sulphuric acid are not mixed in the burette, since this might break on account of the great heat developed. The same chromic acid solution can be used repeatedly (see also p. 12).

The Pyknometer.

The most exact and most generally used instrument for the estimation of specific gravity is the pyknometer, a cylindrical glass vessel with one or two capillary exit tubes; these are graduated with one or several marks.

The most practical form of the instrument is that shown in Fig. 7.* It is suspended from the balance by means of a wire. It has two exit tubes of different widths; the wider tube is graduated with one or more marks. Both tubes must terminate sharply in smooth openings. The pyknometer is filled by suction so that the narrow tube and the vessel itself are completely filled with liquid and the meniscus stands at some point in the wider tube. The meniscus can then be fixed accurately at one of the graduated marks either by sucking out liquid by touching the opening at the narrow end with a small piece of filter paper, or adding it by touching the same opening with a small drop of the liquid on a glass rod; the meniscus moves only in the wider tube where the capillary resistance is trifling.

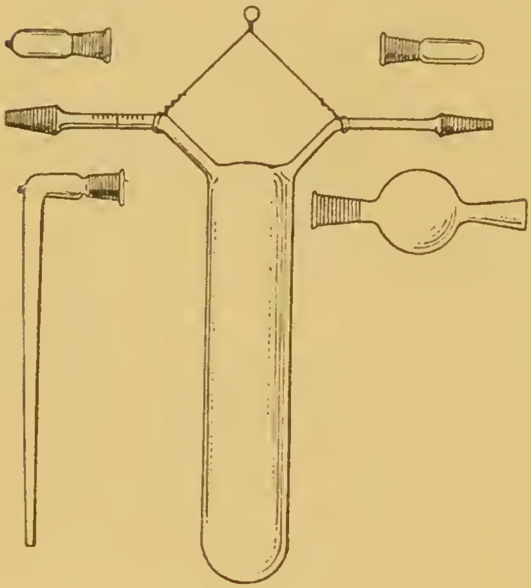

Fig. 7.

The pyknometer, filled with liquid, is hung in a small glass frame in a water bath of constant temperature, until the meniscus no longer alters but remains fixed at a definite point. If very volatile substances are used, the losses due to evaporation while the pyknometer is in the water bath, and during drying and weighing are guarded against by affixing two ground-on glass caps; it is best that the wider tube and the cap which belongs to it are furnished with corresponding marks. When working with aqueous solutions the use of caps is unnecessary. For suitable cases the student himself can make, by help of a blowpipe, a syphon tube and bulb tube, with small pieces of tubing ground on as caps. The simple form without ground-on caps (see Fig. 7*a*) suffices for by far the most cases, and can be made by anyone without difficulty. It is filled by sucking through a piece of rubber tubing. It is advisable to construct it with not one, but several marks, which are most conveniently millimetre divisions. Such an instrument is more easily adjusted, and, if its expansion due to temperature is known, it can be used to estimate the expansion coefficient of the liquid without a second weighing. The outlet tubes must not be immersed in the water bath, but can be taken as at room temperature; it is then only necessary to use the wire as a handle and so avoid warming the pyknometer by contact with the hand.

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* This is easier to clean externally and less fragile than the form proposed by Ostwald.

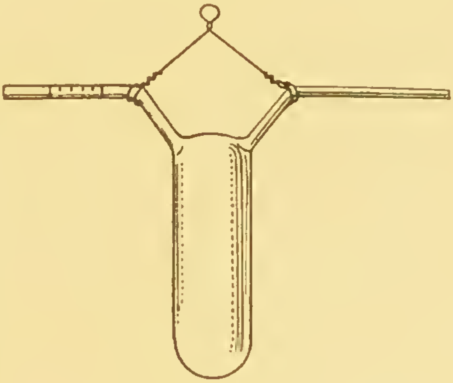

FIG. 7*a*.

A pyknometer with large body and very fine capillary corresponds exactly to a thermometer, and consequently is liable to all the sources of error of that instrument (see pp. 9—11). The correction for the projecting capillary is always negligible. For very accurate work it must be noted that a graduation gives a value slightly too small after the space of a year (corresponding to the rise in the zero point of the thermometer). In all cases pyknometers are sensitive to rapid heating (cp. the after-effect in the case of the thermometer). Hence, inaccuracies arise when the pyknometer is cleaned by rinsing it with methylated spirit and then drying in a current of hot air. The instrument is either kept in a moist condition, and, before using, rinsed out with a few drops of the solutions under examination, or rinsed out by alcohol, and this removed by continuous suction by means of a powerful water-pump.

With pyknometers of Jena-glass the after-effect is trifling and passes quickly.

Using a pyknometer of about 15 c.c. capacity, with careful work densities can be determined accurately to about 0·002 per cent.; to effect this it is necessary that the manipulations during drying, bringing to constant temperature, and weighing are exactly similar when water is taken or the substance whose density is to be determined.

Air dissolved in a liquid scarcely affects its density to a perceptible extent; it is negligible provided bubbles are not disengaged when the liquid becomes warmed.

Accurate Formula.

Let the water content of the pyknometer at temperature t° weigh W grams, the specific gravity of water at that temperature be Q; let the corresponding quantity at t'° of the liquid whose specific gravity is to be examined be F, and x the unknown specific gravity. Then:—

$$x = \frac{F}{W}(Q - 0{\cdot}0012)\left(1 + \frac{t - t'}{40000}\right) + 0{\cdot}0012.$$

The expression $\dfrac{Q - 0{\cdot}0012}{W} = C_t$ is called the pyknometer constant for the temperature t. The figure 0·0012 is the density of air at room temperature. A more accurate estimation of temperature and pressure is unnecessary, since the error of weighing makes the fifth decimal place uncertain.

$\frac{1}{40000}$ is the expansion coefficient of glass; the real figure lies between 0·000019 and 0·000026 according to the kind of glass.

Proof of the Formula.—First, let $t = t'$; neglecting the air displacement $x = \dfrac{FQ}{W}$. Let the weight of air displaced while F and W are determined be λ. Then—

$$x = \frac{F + \lambda}{W + \lambda}Q;\ \lambda = \frac{0{\cdot}0012\,(W + \lambda)}{Q};\ \lambda = \frac{0{\cdot}0012\,W}{Q - 0{\cdot}0012}.$$

$$x = \frac{F + \dfrac{0{\cdot}0012\,W}{Q - 0{\cdot}0012}}{W + \dfrac{0{\cdot}0012\,W}{Q - 0{\cdot}0012}}\,Q = \frac{Q}{W}\,\frac{F(Q - 0{\cdot}0012) + 0{\cdot}0012\,W}{Q}$$

$$= \frac{\mathbf{F}}{\mathbf{W}}(\mathbf{Q} - 0{\cdot}0012) + 0{\cdot}0012.$$

At the temperature t' the volume of the pyknometer has increased to an extent $1 + \left(\frac{t' - t}{40000}\right)$; hence the density $\frac{F}{W}$ must be divided by that factor, or multiplied by $1 + \frac{t - t'}{40000}$.

Problem.—Estimate the specific gravity of a water-alcohol mixture and calculate the percentage of alcohol from Mendelejeff's table (see Landolt-Börnstein).

The expansion coefficient of glass should be determined as a control experiment by weighing at two temperatures differing by ten or fifteen degrees.

$$a = \frac{\left(\dfrac{C_t}{C_{t'}} - 1\right)}{t' - t.}$$

Density of Solids.

When the specific gravity of a solid is less than three, the *suspension method* is most suitable. Two miscible liquids are used which do not react with the substance, and whose specific gravities are such that that of the solid lies between them. A mixture is found by trial, in which the solid—completely free from air bubbles—swims, *i.e.*, it is in hydrostatic equilibrium with the liquid in all parts of the vessel. The specific gravity of the liquid is then found by one of the methods already described, most conveniently by immersing the float of a small Mohr's balance in the same vessel.

Exercise.—Determine the specific gravity of naphthalene. Use as liquids solutions of calcium chloride of about 10 and 20 per cent. (Why not water and the concentrated solution?)

If the specific gravity of the solid is so high that no suitable heavy liquid is available, an attempt must be made to determine the volume of the solid and to calculate the density from the ratio of weight to volume. The sources of error of the method lie in the volume measurement; this cannot be carried out so accurately as a weight determination.

A specific gravity bottle of the form shown in Fig. 8 is employed as most suitable for the object in view. It is first weighed filled with liquid, and then this is displaced in part by a weighed quantity of powdered solid. The liquid employed must be without action on the solid. If the solid obstinately retains air bubbles, it is poured into the dried, weighed pyknometer, and the whole again weighed; then a small quantity of water is added, the pyknometer placed in a vacuum desiccator, evacuated, and then filled completely with water. The following method is recommended:—Through the rubber stopper of the desiccator cover passes a dropping funnel; the lower end is somewhat drawn out, and the point is directly above the pyknometer opening. Evacuation is carried out somewhat slowly, while the liquid is allowed to enter the pyknometer drop by drop.

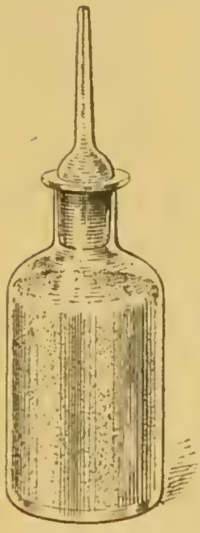

FIG. 8.

If the pyknometer can contain F grams of liquid of specific gravity Q, and if its contents weigh P grams, when it contains liquid plus m grams of solid of volume x, then

$$x = \frac{F - P + m}{Q}$$

and the specific gravity of the body is $\frac{m\,Q}{F - P + m}$.

The accuracy of the method is not great enough to need a correction to vacuo; care must be taken, however, that the temperature is constant during both weighings, otherwise the temperature change would enter into the calculation. (How?)

Exercise.—Determine the specific gravity of a metal (a bar of zinc or copper or some similar metal). Calculate the atomic volume. For other methods (volumenometer, Jolly's capillary balance, etc.) physical text-books must be consulted.

CHAPTER III

DETERMINATION OF MOLECULAR WEIGHTS IN SOLUTIONS

Osmotic Pressure. Depression of Vapour Pressure.

Van 't Hoff has shown that the gas laws apply to dilute solutions. The molecular volume of a gas V is replaced by v, the number of litres in which one gram-molecule of the substance is dissolved. To the pressure of the gas P corresponds the osmotic pressure p, proportional to the concentration. This is the hydrostatic pressure exerted on a boundary wall separating solution and pure solvent, if the wall is permeable for the solvent but not for the solute. As with gases, the gas law, strictly speaking, is applicable only for very dilute solutions, *i.e.*, for large v and small p. Similarly also, if different independent substances are dissolved in the solution, the total osmotic pressure is the sum of the partial osmotic pressures. Hence, if a solute is dissociated electrolytically, the osmotic pressure rises, as does the gas pressure in the case of dissociation produced by the application of heat.

Osmotic pressures can neither be measured accurately nor quickly.

If a substance is dissolved in a suitable solvent, the vapour pressure of the solvent will be lowered, and if small quantities of solute are used, this depression will be strictly proportional to the concentration, and hence to the osmotic pressure of the solution.

The relative lowering of the vapour pressure $\frac{p - p'}{p}$ is equal to $\frac{n}{N}$, if n molecules (or ions) of substance are dissolved in N molecules of solvent.

A gram of urea (molecular weight 60) would give only half as big a depression as a gram of common salt (molecular weight 58·5), because the latter in dilute solutions is dissociated completely into two ions, Na· and Cl′. A gram of acetic acid (molecular weight 60), which dissociates weakly, would give a depression intermediate between the two values.

Just as in the measurement of osmotic pressure the separation wall is only permeable to the solvent, so it is here assumed that only molecules of solvent evaporate—in other words, that the separation film between liquid and gas space is also semi-permeable. But the depression of vapour pressure is also very difficult to measure.

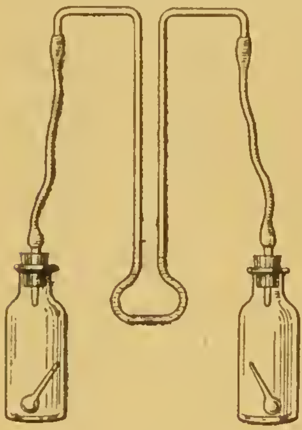
Fig. 9.

The following simple experiment shows qualitatively that a depression does exist:—

Blow two small bulbs of about the same size from thin pieces of glass tubing, drawing out the open ends into capillaries. Into the one bulb, by alternate warming and cooling, transfer 3 or 4 c.c. of ether, and draw off the capillary. Into the second transfer a similar amount of a roughly six per cent. solution of benzoic acid in ether, and seal this also. Place each bulb carefully in glass bottles, each of about 200 c.c. capacity (see Fig. 9), and closed with rubber corks penetrated by short pieces of glass tube. These two tubes are then connected by rubber tubing with the two ends of a manometer, the lower part of which contains coloured water. At the commencement of the experiment make sure that the water stands at the same level in both sides of the manometer, and if necessary adjust the levels by pushing in one or other of the corks more tightly. When this precaution has been attended to, break both bulbs simultaneously by strongly shaking both vessels. During this operation the rubber tubes should be pinched with the fingers. On releasing the pressure on them, so that vapour can pass, it will be seen at once that the coloured water stands higher on the side of the manometer nearer the solution, showing that the pure solvent has the higher vapour pressure.

Depression of Freezing Point. Elevation of Boiling Point.

Since the methods just mentioned are so difficult in practice, in laboratory work and exercises only the following two methods are used to determine the molar weight of dissolved substances: measurement of the depression of the freezing point (cryoscopic method) and of the elevation of the boiling point (ebullioscopic method).

The boiling point is defined as the temperature at which the vapour pressure becomes equal to atmospheric pressure, the freezing point as the point at which ice and water, or more generally solid and liquid solvent, have the same vapour pressure. The diagram (Fig. 10) shows the connection between the temperature and vapour pressure of ice (thick line), water (thin line) and solution (dotted line). It is seen that a diminution of vapour pressure is accompanied by depression of the freezing point, and also by elevation of the boiling point. It will also be observed that for the same concentration the depression of the freezing point must be greater than the elevation of the boiling point. Indeed, it is possible to calculate these values. Let p be vapour pressure of the pure solvent at the temperature of the boiling solution T', and p' the vapour pressure of the solution at the same temperature. Then for a dilute solution:—

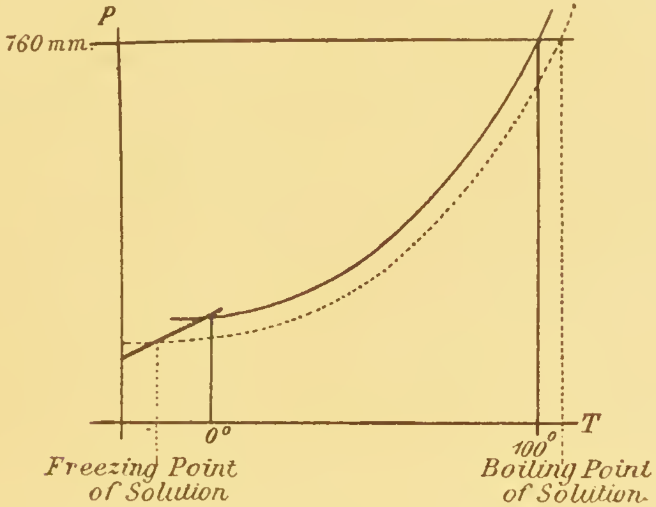

FIG. 10.

$$T' - T = (p - p').\frac{dT}{dp}.$$

According to the well-known formula of Clausius, which follows from the first and second laws of thermodynamics

$$\frac{dp}{dT} = \frac{Q}{(v - v_1)\,T}$$

where Q is the molecular heat of evaporation; since v_1 the volume of the liquid, is exceedingly small compared with the volume it occupies as vapour v, and since $v = \frac{RT}{p}$, therefore

$$\frac{dp}{dT} = \frac{Qp}{RT^2},$$

hence
$$T' - T = \frac{p - p'}{p} \cdot \frac{RT^2}{Q}.$$

Now it has been shown that $\frac{p - p'}{p}$, the depression of the vapour pressure, is equal to $\frac{n}{N}$, the ratio between the number of molecules of solute and solvent. If c molecules of solute are dissolved in 1000 grams of solvent, then

$$T' - T = \frac{c}{1000} \cdot \frac{RT^2}{q}$$

where q is the *specific* heat of evaporation.

An exactly analogous calculation holds for the depression of the freezing point.* In both cases it is assumed that (*a*) the solutions are dilute, (*b*) only the solvent and not the solution changes into the second state of aggregation. (Compare the latter assumption with that of the semi-permeability of the membrane used in the measurement of osmotic pressures.)

The above equation can be written

$$T' - T = \Delta = \left[\frac{RT^2}{q\ 1000}\right] c.$$

The expression within the brackets is called respectively the molar depression of the freezing point, and the molar elevation of the boiling point, and is a characteristic constant of the

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* The formula can be written in such a way that the work can be calculated, which is performed by concentrating the solution through removal of the solvent. This work completely corresponds to the work done in compressing a gas, *i.e.*, $RT \ln \frac{p_1}{p_2}$, except that the gas pressure is replaced by the osmotic pressure. The student should convince himself that the work magnitude pdv is involved in the above formula. By a simple transformation the expression is obtained

$$(p - p')(v - v_1) = Q \frac{T' - T}{T}.$$

The work magnitude is concealed in the final form

$$T' - T = \Delta = \frac{RT^2}{Q} \frac{c}{1000}.$$

solvent (k). To calculate the molar depression of the freezing point for water, cp. note, p. 2 ($q = 79\cdot7$ cal. at 15°).

TABLE I.

Solvent.	Molecular Elevation of Boiling Point.		Molecular Depression of Freezing Point.	
Water	0·52°	(100°)	1·86°	0°
Alcohol	1·15°	(79°)	—	—
Benzene	2·67°	(80°)	5·0°	(+ 5°)
Glacial Acetic Acid	—	—	3·90°	(+ 17°)
Naphthalene	—	—	6·9°	(+ 80°)
Carbon Disulphide	2·37°	(46°)	—	—
Ethyl Ether	2·11°	(35°)	—	—

If the molar weight of a dissolved substance is to be determined, the equation is written in the form $\Delta = kc$. If the solution contains a grams of solute in 1000 grams of solvent, the molar weight of the solute is $M = \frac{ka}{\Delta}$. If the observed molar weight M' is smaller than that required by theory, dissociation is indicated; for a binary electrolyte the percentage of dissociation is $\left(\frac{M}{M'} - 1\right) \times 100$. If M' were found larger than required by theory, association would be indicated.

From the above it is obvious that we measure directly, not the molar weight, but Δ, proportional to the ratio $\frac{n}{N}$, the number of dissolved molecules to that of molecules of solvent. If, consequently, the dissolved substance combines with one or more molecules of the solvent (*e.g.*, by the formation of hydrates when water is the solvent), then $\frac{n}{N}$, and consequently the depression of freezing point or elevation of boiling point respectively will be slightly altered. In a tenth normal aqueous solution 555 molecules of water are present for one of the dissolved substance. If therefore a decahydrate were formed in the solution, Δ (and the molecular weight calculated from it) would differ by 2 per cent. from the theoretical value. A correction for hydrate formation is therefore unnecessary, since the experimental error usually amounts to about 3 per cent.

The accuracy of the cryoscopic method can only be made much greater by taking special precautions and enlarging the apparatus.

Both the cryoscopic and ebullioscopic methods have been thoroughly and carefully examined and improved by Beckmann, who constructed a thermometer specially for these measurements.

The Beckmann Thermometer (Fig. 11.).

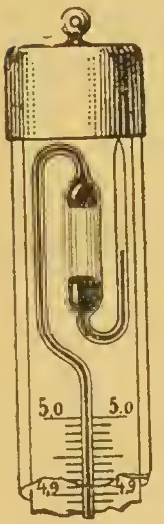

Fig. 11.

In the determination of molar weights, as also in most calorimetric work, it is necessary to determine small temperature differences very accurately. It is obvious that for this purpose the thermometer must consist of a large mercury vessel, with a very narrow capillary. The range need be only a few degrees; in the common type of Beckmann thermometer it is about five or six degrees. The scale is divided into hundredths of a degree, so that readings to thousandths can be made, if the calibration is correct.

In order to use one instrument for different temperatures, the capillary of the Beckmann thermometer is bent twice at right angles, and ends in a pipette-shaped reservoir, the other end of which is similarly bent, and closed. The thermometers are calibrated at 0°; if an instrument is to be used at a higher temperature, it should be heated to about four degrees above the temperature desired, and the back tapped carefully with a flat hand, so that the drop of mercury which hangs on the upper end of the pipette-shaped vessel falls. To use the thermometer at a lower temperature, invert it, tap gently on the back, and so transfer the mercury from the bottom to the top of the reservoir. Bring it to its usual position and heat it to such an extent that the mercury rises to the end of the capillary and joins with the drop at the top of the reservoir. Then place the thermometer in a bath, the temperature of which is two or three degrees above that of the experiment, and, when equilibrium is set up, tap until the rest of the mercury in the top of the reservoir has fallen. If, however, insufficient mercury remains to fill the capillary, the whole procedure must be repeated. The transition from capillary to reservoir should be gradual, so that a big drop of mercury can remain on the end of the bent capillary without falling.

Exact results can be obtained with the Beckmann thermometer only if all the precautions are borne in mind which were recommended in the section on the thermometer (p. 9), especially

1. tap gently on the side, and stir regularly;
2. correct the calibration;
3. avoid big changes of temperature during a measurement.

As in all cases where difference determinations are made, both values should be measured in precisely the same manner, without too big a time interval between them.

The following section contains an account of the method for the most important solvent, water. If other solvents are employed, additional precautions must be observed; these will be described later.

The Depression of the Freezing Point.

Beckmann's apparatus (Fig. 12.) consists essentially of a large test-tube with a side tube through which the substance is added. The upper end of the test tube is wider and is closed by a two-holed rubber cork. Through one hole passes the thermometer, while the second is provided with a short piece of glass tubing to act as guide for the stirrer. The stirrer consists best of a glass rod on which a platinum ring is sealed. The test-tube with its contents is fixed in a wider tube by means of a cork ring. The second tube serves as an air jacket and the inside should be kept carefully dry. The jacket rests on the metal cover of a wide glass vessel and is kept in position by three springs. The metal cover has a second hole, through which passes a thick stirrer of brass rod, and a third for a thermometer. The glass vessel is filled with a cooling mixture at a temperature two or three degrees below zero.

After the Beckmann thermometer is adjusted so that at 0° the mercury stands at about the middle of the scale, it is placed in position. By means of a pipette 25 c.c. of water are transferred to the test-tube. The bulb of the thermometer must be well covered by the water, and the liquid in the cooling mixture must stand at a higher level than that in the test-tube.

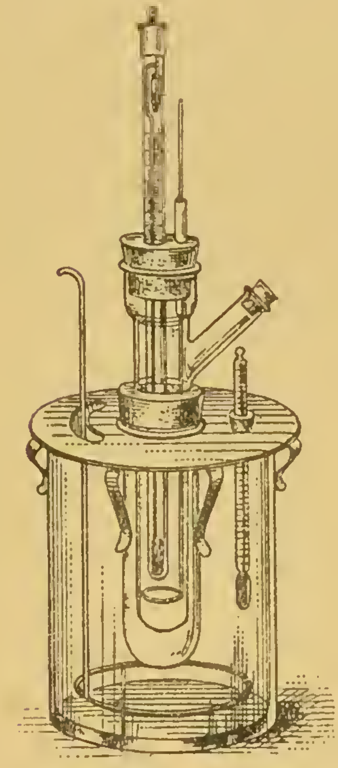

FIG. 12.

While the water is cooling, the substance should be weighed — if possible as a fine powder — in a weighing bottle. Two roughly equal quantities should be weighed, of such a magnitude that each will give a depression of between 0·4° and 0·5°.

The freezing mixture is stirred occasionally, until the temperature of the water has fallen below zero; ice is then caused to separate by sudden and violent stirring, or else a small piece of pure ice is thrown in through the side tube. The mercury in the thermometer rises, and, while the water is stirred regularly, and the thermometer tapped gently, three or four readings are taken with a lens at intervals of half a minute. The test tube and contents is then removed from the freezing vessel, the ice thawed by the warmth of the hand, and—after the exterior of the test tube and the interior of the jacket are carefully dried—a new determination is made exactly in the same way.

After the ice has been melted again, the first portion of the weighed substance is thrown in, and a measurement made as before. The second portion is treated similarly.

If the freezing bath is too cold, the mass of ice in the test-tube increases rapidly, and with it the concentration of the solution. As this takes place, the freezing point slowly sinks. In such a case the highest reading is the most correct. If the degree of super-cooling is known the (initial) mass of the separated ice can be estimated. Since the heat of fusion of ice amounts to eighty calories, and the specific heat of the solution is about 1, super-cooling to the extent of 1° concentrates the solution about 1·25 per cent. This does not include the amount of ice separated in the course of measurement.

Exercise.—Determine the molecular weight of urea, or cane sugar, and the amount of dissociation of common salt.

Remarks.—In this primitive form the method is not very accurate. The chief cause of error arises from the freezing bath, which—for practical reasons—in this case is made too cold. Even with rapid stirring a difference of temperature of some tenths of a degree would suffice to compensate for the heat of stirring and that derived from external sources. The lower the temperature of the freezing bath, the lower will be the apparent freezing point. The influence of the bath can be compensated, if the solution and ice are so stirred as to expose the greatest possible surface to each other, and are kept well mixed.

Efficiency depends not on the amount of ice, but on the amount of surface exposed. The ice froth, as it separates from the solution, produces a better effect than the leaves or spicules which form in pure water. If a large amount of pure, finely divided ice has separated, the temperature reading is trustworthy, but, on the other hand, the estimation of the concentration from the weighed quantity of solid added, and the amount of water used, is no longer certain. Hence in exact work, a quantitative analysis of the solution permanently in equilibrium with the ice is indispensable. As in the case of all calorimetric measurements, the degree of exactitude increases with the amount of solution employed. With large quantities of liquid, mechanical stirring of liquid and freezing mixture are essential.

If **organic solvents** are employed, the temperature of the freezing mixture must be regulated in other ways, but it must never be more than two or three degrees colder than the freezing point of the solvent.

If a solvent is very *hygroscopic* (*e.g.*, glacial acetic acid), no measurements are possible by the method described, since damp air is continually forced through the apparatus as it is stirred. Hence the glass guiding tube is connected with the glass stirring rod by a piece of wide thin-walled rubber tubing, tightly wired to both tube and rod. Or else the guiding tube is connected with a bulb apparatus of the form shown in Fig. 13, and well-dried air passed through the apparatus. The tube connecting the two bulbs contains a few drops of concentrated sulphuric acid, which is prevented from spirting over by the small plate of mica fused on to the side of the bulb.

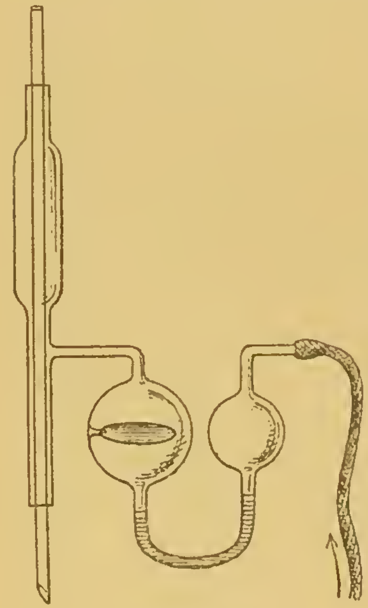

FIG. 13.

The following arrangement is more elegant than that by which a piece of the frozen solvent is thrown into the apparatus through the side tube. A narrow glass tube ending in a capillary is dipped into a thin-walled test tube containing a little solvent, and held in position by a tightly-fitting cork. The tube is immersed in the freezing mixture. When it is desired to freeze the solution, the capillary tube is stuck through the side tube of the freezing vessel, and the stirrer is lifted so far that the part which usually dips into the liquid touches the end of the capillary. Since the latter contains solid solvent, and the layer of liquid on the stirrer is supercooled, this freezes immediately, and on stirring causes a regular distribution of finely-divided solid throughout the whole solution.

Abnormal Molecular Weights.

Many organic solvents, especially, of those in common use, benzene and naphthalene, give for organic substances containing hydroxyl groups values of the molecular weight which depend largely on the concentration. The values are too great for concentrated solutions, and decrease, with dilution, to the theoretical figure. This phenomenon is due to the formation of associated molecules, such as occur in certain vapours (S_8, P_4, H_2F_2, etc.). Solvents which contain hydroxyl groups have a greater dissociating power than benzene and naphthalene, and give the normal value. If, consequently, the molecular weight of an organic substance is under consideration, several determinations at different concentrations are always made; the molecular weight increases with increasing concentration. By extrapolation the value is found for infinitely great dilution. The molecular weight of binary electrolytes in water can be found in a similar way, by doubling the extrapolated value corresponding to infinitely great dilution. An abnormal result arising from a similar source is that where a solid solution of solvent and dissolved substance separates; this, however, cannot be taken into consideration here.

Exercise.—Determine the molecular weight of paranitrophenol in naphthalene and acetic acid at several concentrations.

Elevation of the Boiling Point.

This method is less convenient than the cryoscopic, since the temperature differences to be measured are smaller, and it is much more difficult to avoid super-heating than supercooling. Again, since much higher temperatures are necessary for this method, the exchange of heat with the surroundings is much greater. Boiling points vary largely with the pressure, whereas the variation is negligible in the case of freezing points. A number of different types of apparatus have been proposed to avoid these numerous difficulties. Of these only two forms constructed by Beckmann are described here.

Apparatus for Direct Heating (Fig. 14).

The boiling vessel, a large stout-walled test tube with two side tubes, fits inside a porcelain or glass jacket, which contains some of the boiling solvent. In this way the exchange of heat with the surroundings is lessened. Small mica windows in the jacket permit observation of what takes place in the boiling tube. Through the bottom of the latter is sealed a stout platinum wire, of which the outer end penetrates the small circular asbestos disk on which the tube rests, and in this way transmits heat to the interior. A layer of garnets or platinum tetrahedra is placed inside the boiling tube to prevent super-cooling, and small pieces of unglazed earthenware serve the same purpose in the jacket. Both boiling vessel and jacket have side tubes fitted with condensers. The second side tube in the boiling tube serves for the introduction of the substance. The bulb of the Beckmann thermometer should be protected from direct contact with cooled drops of solvent from the condenser, by means of a roll of pure silver foil; the protected bulb rests on the garnets or platinum tetrahedra. If there is much free space between the jacket and the boiling tube, the latter should be surrounded by asbestos paper. The boiling tube itself is heated by a small pointed flame, the jacket by a ring burner. Both flames must be regulated to produce a brisk but regular boiling. A tripod and suitably shaped asbestos case are usually provided with the apparatus.

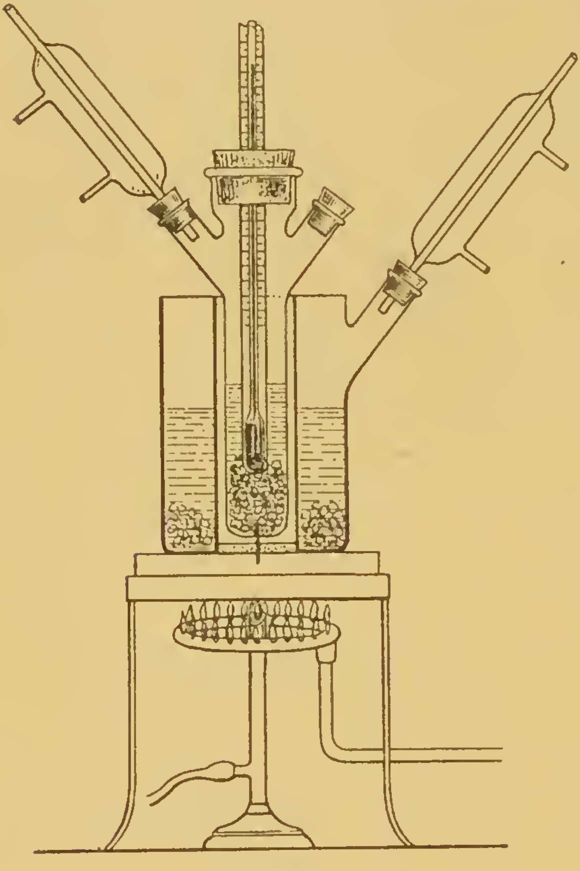

Fig. 14.

A small part of the solvent is in the vapour phase, and therefore does not count as solvent, resembling in this respect the solid phase in the cryoscopic method; the method is not sufficiently accurate to necessitate a correction. Generally speaking, agreement in consecutive readings to a few thousandths of a degree is sufficient, and it is better to make a number of independent readings—by fresh additions of substance—than to enlarge the number of readings for each addition. The hot liquid dissolves the solids very rapidly, so that these can be added in the form of pastilles or small pieces; elaborate weighings by difference in a weighing bottle are consequently unnecessary. The solvent is added to the boiling tube by means of a calibrated pipette. The solute, if liquid, can be added by means of a pipette, which, weighed before and after, gives the amount of liquid added. If organic solvents are employed no rubber corks should be used.

Apparatus for Heating by the Passage of Vapour.

The danger of super-heating and the necessity for heating both jacket and boiling vessel can be got rid of by heating the latter in a current of vapour. If the vessel in which the current of vapour is produced is placed outside the boiling tube, it protects it in this way with a vapour jacket. It seems paradoxical to heat an aqueous solution to a temperature above 100° by means of steam at 100°. But since an aqueous solution must be at a temperature above 100° in order to be in equilibrium with steam at 100°, the solution must heat itself to above 100°; the energy required for that purpose is supplied as heat of condensation by the condensing steam. Of course the solution becomes more and more dilute as the experiment proceeds, and its concentration can be determined only when an equilibrium is reached; with resulting constant temperature. At this point readings taken at half-minute intervals should agree; the experiment is completed by interrupting the current of steam.

The recent form Beckmann has given to this apparatus is shown in the figure. The boiling tube *B* is sealed into the vapour jacket *V*; it has three side tubes with ground joints, one for the thermometer *T*, a second for the condenser *C*, and a third for the introduction of substance. Another side tube near the bottom allows the vapour to enter through the solution. The vapour jacket when in use is not connected with the atmosphere, so that the vapour evolved must pass through the solution. The ground joint connecting the condenser with the apparatus contains a hole which, on rotating, connects the vapour jacket with the external atmosphere through the tube *R*, and *C*. *S* is a safety tube ground into the jacket, and contains a groove near *G* which can be caused to coincide with the hole *O* in the side tube itself ; in this way the pressure can be adjusted. The boiling tube is graduated in millimetres, and should be calibrated before using by additions of water from 5 or 10 c.c. pipettes through the side tube *Q*. The thermometer must be in place before this is done, and must not be disturbed after the calibration until the end of the experiment. The first pipette content must fill the vessel above the first

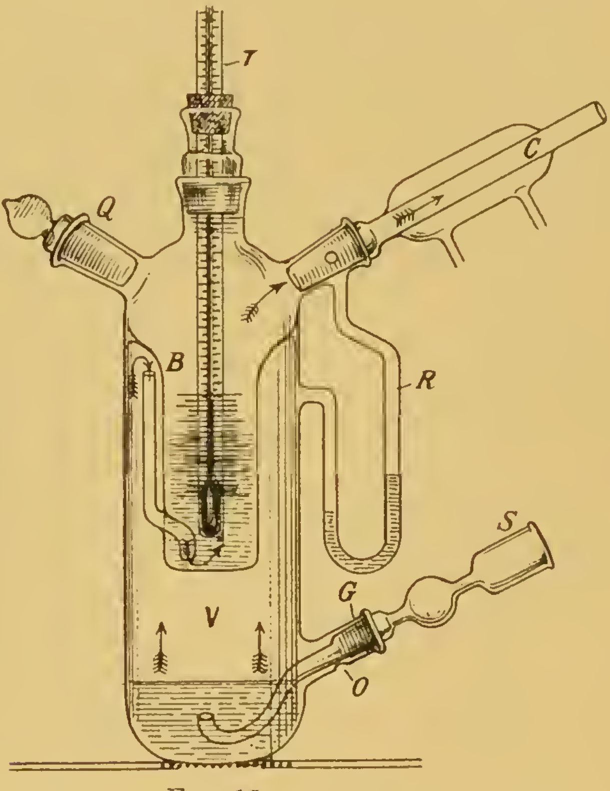

FIG. 15.

division and the under part of the mercury bulb of the thermometer. The further quantities are then employed to calibrate the cylindrical ring space between the walls of the vessel and the thermometer. Then the volume corresponding to each scale division is known. It is necessary to take into account the density of the boiling solution, if this differs greatly from unity, since the values for the molecular elevations of boiling point given in the table on p. 41 refer to one gram molecule in 1000 grams (and not in 1000 c.c.) of solvent.

It is advisable not to cool the condenser with running water, unless the solvent is valuable, inflammable or possesses a very noxious odour. The temperature of the boiling vessel is always disturbed by the cold condensed drops falling back; moreover the volume of liquid increases to too great an extent.

The whole apparatus is mounted on a small piece of wire-gauze, fixed in an asbestos plate, and is heated with a small pointed flame. While the solvent is slowly heated, small pieces or pastilles of the solute under investigation should be weighed accurately. When the solvent is boiling regularly, half-minute readings of the thermometer are taken (in every case preceded by gentle tapping), until three successive readings give values not differing by more than 0·002°. Without interrupting the boiling, a weighed pastille is introduced through *Q*, and readings again taken until constancy is reached. The stopper *Q* is then removed, and *S* turned so that *G* coincides with *O*, so that both boiling tube and vapour jacket are in direct connection with the atmosphere. Then, but not till then, the flame is removed, and the level of the liquid is read on the scale. The second experiment with the second quantity of solute is carried out in the same way.

Exercise.—Determine the molecular weight of cane sugar and sodium chloride in water, and of potassium iodide in absolute alcohol (the latter illustrates *weak* dissociation).

CHAPTER IV

THERMO-CHEMISTRY

Calorimeters. General Remarks.

For calorimetric exercises other than determinations of the heat of combination, home-made calorimeters, put together from large beakers, are sufficiently good.* To lessen exchange of heat with the surroundings, the real calorimeter beaker is protected by an air jacket; with the help of three small pieces of cork shaped as knife edges, and affixed with sealing-wax, it is placed inside a larger beaker. The air between both beakers is kept dry. The outer one is provided with a wooden cover, containing a hole for a Beckmann thermometer, one for a stirrer, and a third for the small glass vessel containing the reacting substance.

If a metal stirrer is used, the handle must be covered with a cork, to prevent transference of heat from the hand to the calorimeter. A glass stirrer must have its end flattened. A short piece of glass tubing fixed in the hole acts as a guide for the stirrer and protects the wooden cover from liquid. It must be sufficiently large to permit free movement of the stirrer.

The **water equivalent** of a body is the amount of water to which addition of the same quantity of heat will produce the same rise of temperature. It is equal to the mass multiplied by the specific heat of the substance, since by definition the specific heat of water is unity. The water equivalent of a calorimeter (vessel, stirrer, thermometer, and liquid) is determined by one of three methods. In the first the mass of each part is multiplied by its specific-heat and the products added (see Table IV.). In the second method the calorimeter is calibrated by introducing a known quantity of heat in the form of a previously heated body. Thirdly, the heat can be added by an electrical method (described later); this method is the most exact and elegant of the three. For preliminary work the additive method is often sufficiently accurate.

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* The use of a Bunsen ice calorimeter is certainly too complicated for an elementary course. It possesses the great advantage, however, that it is independent of the temperature of the surroundings, and gives an absolutely constant temperature.

The unit of heat or *caloric* is defined as that quantity which raises one gram of water *from* 14·5° *to* 15·5° C. in temperature.* Between 10° and 30° C. the specific heat of water only changes slightly; at ordinary temperatures it may be taken for practical purposes as unity.† The water equivalent of the thermometer can be found approximately as follows:—By means of a measuring cylinder find out how many c.c. of the thermometer dip into the liquid in the calorimeter. Glass conducts heat badly, hence that part of the thermometer which is not immersed does not take part in the temperature change. Mercury is a good conductor, but the small amount in the capillary can be neglected. Of course, the bulb of the thermometer must be completely immersed. Multiply the volume thus found by 0·46; it will be seen from the tables that the water equivalents for 1 c.c. of mercury and 1 c.c. of glass are by chance both equal to 0·46.

The specific heat of solid metals can be calculated roughly from the Dulong-Petit law. (Brass, copper, and zinc have the same specific heats.)

The water equivalent of the calorimetric vessel itself has been considered above: that of the jacket is neglected. If the stirrer has a long stem, two-thirds the weight should be used in calculating its equivalent. The specific heat of an aqueous salt solution can be taken as equal that of the water in the solution without introducing a large error.

The slight error introduced in each of these products is lessened by observing the very important rule: make the weight of the water used large in comparison with the total weight of the other parts, since the specific heat of water is the unit.

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* The unit formerly employed was the *mean* or 100° calorie, *i.e.*, the one-hundredth part of the amount of heat required to raise one gram of water from 0° to 100°; it is by chance almost equal to the present unit, defined above.

† In the exercises which follow distilled water need not be used unless specially mentioned.

Heat Exchange with the Surroundings.

The heat exchange of the calorimeter with the surroundings either by radiation or conduction is never negligible. This is true even when the old Rumford method is used where the initial temperature is chosen as much under (or over) the room temperature θ_0 as the temperature at the end of the reaction is over (or under) θ_0. Here the heat exchange is proportional to the temperature difference $\theta_0 - \theta$ and the time t; it is $\int (\theta_0 - \theta)\,dt$. The thermometer does not register a temperature change immediately, but lags behind. Hence the observed temperature variation is at first rapid, then slower and slower; the room temperature is reached rapidly; the second period is much longer; $\int (\theta_0 - \theta)\,dt$ is much larger in this interval. Thus the heat gained from (or lost to) the surroundings in the first period is not equal to the heat lost to (or gained from) them in the second; an error is consequently introduced. The correction is made preferably in the following manner:—

Before starting the reaction determine the rate at which the thermometer is changing by stirring regularly, tapping the thermometer continually, and taking readings every half-minute. Then start the reaction, and observe the time which elapses before the reappearance of the regular velocity of the temperature change. Halve this time, and imagine that the reaction is compressed into the point of time thus found. Extrapolate from the two temperature gradients what would have been the temperature in each case had no reaction taken place. The two values can be obtained best graphically: a typical example is shown in Fig. 16. As abscissæ are plotted the times, as ordinates the temperatures, one division represents respectively one minute and 0·1 degree of the Beckmann thermometer. On the latter 1·40 is the room temperature. As will be seen from the diagram, the curve showing the temperature change has different direction before and after the reaction; the room temperature lies between the initial and final temperatures; it happens in this case that it is about the mean of the two. Even then it is seen that the values $\int (\theta_0 - \theta)\, dt$, *i.e.*, the two shaded portions in the diagram, are not equal. Rumford's correction, applied in this case, leads to a result too small by about 0·06°, because the fall in temperature during the second half is much greater than the rise during the first half. It is also apparent that the thermometer does not begin to rise immediately the reaction commences (at 2·5 minutes), but half a minute later. Again, the apparent constancy of temperature after seven or eight minutes must be guarded against. It is in reality but a flat maximum; this always results when two differently directed effects balance each other momentarily. Observations must be continued till the temperature change becomes steady. In the example shown in the diagram the calculation is based on the assumption that reaction and heat exchange took place completely at the time 5·5 minutes.

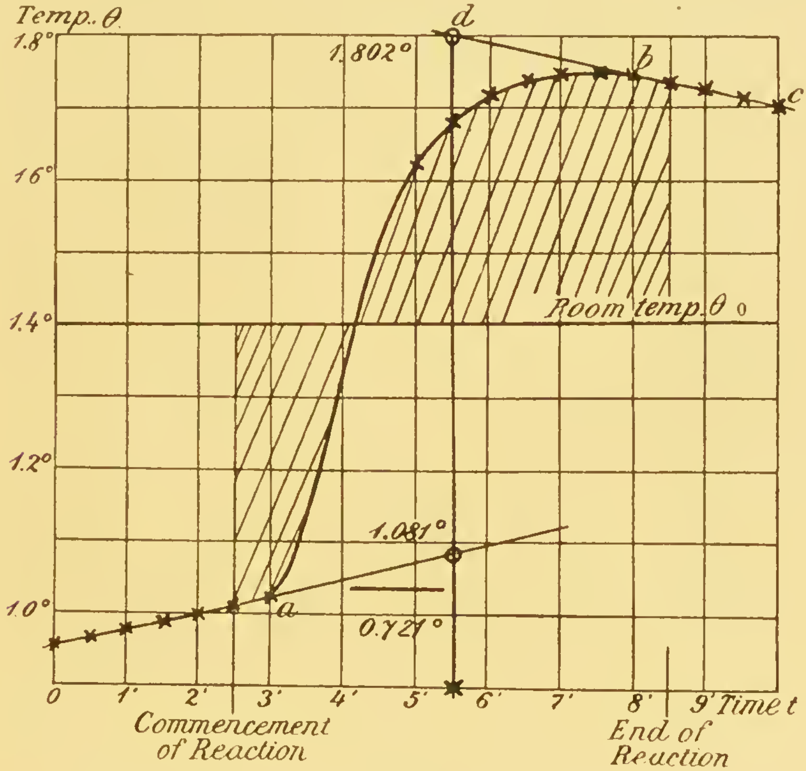

FIG. 16.

Provided the temperature changes regularly, and not too quickly, the method described affords exact results, even at temperatures far removed from that of the room, where the change is in the same direction before and after the reaction.

With regard to the quantity of material to be employed in such experiments, the following consideration is of importance. It is under all circumstances safer to work with small quantities, measuring a small change of temperature accurately by means of a good Beckmann thermometer, than to measure a big change with a less accurate instrument. In any case the change measured should never be greater than 2°. If a large evolution of heat cannot be avoided, a correspondingly large amount of water must be used. Under ordinary circumstances 500 grams of water will suffice; with regular stirring the exactitude increases with the dimensions of the calorimeter.

1. Determination of Specific Heat by the Method of Mixtures.

If the substance is soluble in water, it is placed in a glass or metal tube of as small water equivalent as possible; if insoluble it is suspended directly inside the metal tube (Fig. 17), heated by the surrounding steam-jacket to 100°, then, after the cork beneath has been removed, by means of the silk fibre suspension the substance is allowed to fall rapidly into the calorimeter through the hole in the wooden cover. A necessary precaution is to keep the heating apparatus at some distance from the calorimeter until the actual moment of transference.

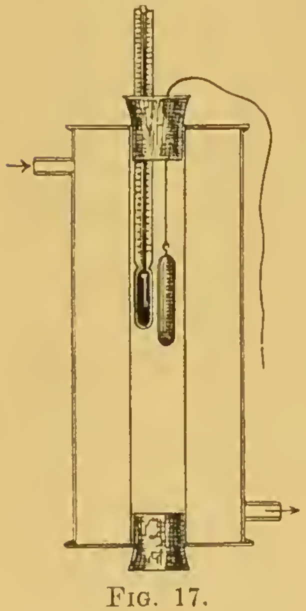

Fig. 17.

If it is remembered that the amount of heat lost by the substance equals that gained by the calorimeter, the calculation is simple. If the water-equivalent of the calorimeter be W, the corrected initial temperature t_1, the corrected final temperature t_2, and if the substance under investigation possess weight G, and its initial temperature be T, then its specific heat x follows from the equation—

$$G \, . \, x \, . \, (T - t_2) = W \, (t_2 - t_1) \, ;$$

$$x = \frac{W \, . \, (t_2 - t_1)}{G \, . \, (T - t_2)}.$$

Exercise.—Determine the specific heat of lead and copper, and of KCl or $PbCl_2$. Calculate respectively the atomic and molecular heats. (Dulong and Petit's and Kopp and Neumann's Law.)

Select amounts of substance and of water, which will give a rise of temperature of between 0·3 and 0·6 of a degree.

2. Heat of Solution.

The substance, finely powdered, is placed in a thin-walled test tube along with a glass rod. The test tube is hung through the third hole of the calorimeter cover, already mentioned. Both test tube and glass rod must be considered in calculating the water equivalent of the system. The apparatus is allowed to stand for a quarter of an hour, in order to allow its temperature to reach that of the surroundings. Then the rate of change of temperature is observed; when this becomes quite regular, the glass rod is pushed through the bottom of the test tube. The temperature change is measured as already described.

The heats of mixing, hydration, precipitation, and dilution can be measured in a similar manner.

Exercise.—Determine the heat of solution of Glauber's salt ($Na_2SO_4 + 10H_2O$) and of NaCl.

Remarks.—1. When Glauber's salt is dissolved, a large amount of heat is absorbed, with common salt scarcely any. Accordingly, from the principle of least resistance* we expect the solubility of the former to increase greatly with rise of temperature, that of the latter but little; such is actually the case. If, on the other hand, using a Dewar vessel, anhydrous Na_2SO_4 is dissolved in water above 33°, there will be a small

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* If a saturated solution of a completely dissociated binary electrolyte has at the absolute temperature T, the concentration c, then

$$\frac{d \ln c}{dT} = - \frac{q}{2RT^2},$$

where q is the heat which the system evolves when one gram-molecule of substance is dissolved (for example see p. 59).

evolution of heat; this agrees with the fact that the solubility of anhydrous sodium sulphate decreases slowly with rise of temperature.

2. To determine the temperature change accurately it is necessary to use as solvent not pure water, but an almost saturated solution of the salt.

3. Changes of heat which cannot be determined directly, *e.g.*, most of the heats of transformation, can often be ascertained indirectly. To measure the heat of transformation of rhombic into monoclinic sulphur, it would be necessary to work at 96°, but the required result is obtained simply by determining the heats of solution of both modifications in the same solvent.

It follows from the first law of thermodynamics that heat evolution is the same whether completed in one stage or more than one. We can imagine that solution of monoclinic sulphur takes place in two stages, at first transformation into the rhombic variety, which then dissolves. The value for the second stage is measured directly in the parallel experiment; consequently the difference in the two values is the heat evolution of the first stage, *i.e.*, the heat of transformation.

The same reasoning holds for solution accompanied by chemical action, *e.g.*, when two modifications of a metal are dissolved in an acid, the same solution and bye-products resulting.

3. Heat of Precipitation of Silver Chloride.

A thin-walled test tube, as in the previous experiment, is taken, and 10 c.c. of a normal solution of $AgNO_3$ are poured into it. Excess of NaCl is dissolved in the water of the calorimeter (about 500 c.c.). When the temperature change has become constant, it is noted, and the reaction started by crushing the test tube. It is usual to calculate the heat of precipitation for one-gram molecule of AgCl.

Remark.—The equation for the reaction, written ionically becomes—

$$Ag^{\cdot} + NO'_3 + Na^{\cdot} + Cl' + aq. = AgCl + Na^{\cdot} + NO'_3 + aq. + Q\,cal.,$$

or without superfluities,

$$Ag^{\cdot} + Cl' = AgCl + Q.$$

Consequently the observed evolution of heat (about 15—16,000 g.cal. per Mol. AgCl) contains not only the heat of precipitation, *i.e.*, the heat of solution with sign reversed, but also the heat of dissociation.* But as the latter has always been found small for strongly ionised salts, by analogy it can be neglected here.

The very large negative value for the heat of transformation found for most of the so-called *insoluble* salts indicates that their solubility increases rapidly with rise of temperature, an effect which is rather important for quantitative analysis. For example, the solubility of AgCl rises between 18° and 34° to double value†, and increases one hundred times between 25° and 100° (see later pp. 140 and 161).

4. Heat of Neutralisation. (Heat of Dilution.)

As an example the heat of neutralisation can be measured between about 20 grams of a roughly twice normal solution of hydrochloric acid and excess of sodium hydroxide or ammonia solution.

This reaction can be commenced in the same way, by breaking a glass tube. It is more elegant, however, to use a weight pipette, of the form shown in Fig. 18, which can be kept closed. The closing is effected by means of a glass rod which passes through the pipette and ends in a small ball; the latter is joined to the exterior of the pipette by a small piece of good rubber tube. It is better if the lower opening of the pipette and the ball on the rod are provided with slightly ground surfaces which fit into each other. The pipette is weighed with its contents and placed in the calorimeter liquid until the temperature change is regular. When this is the case, and the rate has been observed, the glass rod is pushed through, and the pipette raised simultaneously to prevent entry of the

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* Taken quite strictly, the observed heat evolution includes the heat of dilution of $AgNO_3$; this can be neglected.

† Calculate from these data as a control the heat of precipitation by means of the equation (see p. 57)—

$$\frac{\ln \frac{c_2}{c_1}}{T_2 - T_1} = \frac{q}{2RT^2} \text{ ; } \ln 2 = 0{\cdot}693.$$

solution. When it has drained empty it is drawn out, and consequently is not taken into consideration in measuring the water equivalent. At the end of the experiment the pipette is dried externally and again weighed. The titre of hydrochloric acid must be reckoned by weight, not by volume. In the preparation of the sodium hydroxide solution the water is weighed in a rough balance, or measured with a graduated flask, and an excess amount of NaOH (from about a third of a stick) is stirred in. It should be noted that the act of solution is accompanied by considerable heating (heat of hydration, not of solution, since the solubility of the hydroxide increases with rise of temperature). Hence a longer time must elapse necessarily before the temperature equilibrium of the solution is attained completely.

In the velocity of temperature change a small heat effect, such as accompanies the absorption of carbon dioxide from air by the hydroxide solution, is masked. Since, however, an excess of NaOH is employed, the temperature change shows the evolution of heat *following* the neutralisation as well, so that the difference due to this cause is completely negligible.*

To prepare the ammonia solution 5 c.c. of a 25 per cent. solution of ammonia (sp. gr. 0·91) is pipetted into the calorimeter water. How great are the water-equivalent of this ammonia solution and that of the hydrochloric acid solution?

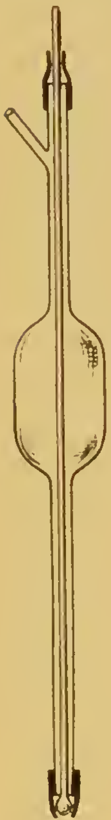
FIG. 18.

The act of neutralisation of concentrated hydrochloric acid solution by dilute soda solution can be considered to take place in two parts—

(1) dilution of the HCl to the final volume of its solution;

(2) neutralisation of this dilute HCl solution, by the NaOH.

Since the first part is accompanied by a small, but distinctly measurable, heat change (the **heat of dilution**), and it is only desired to measure the true heat of neutralisation (really at infinite dilution), the total heat change must be measured, that corresponding to (1) also determined, and the two quantities, both calculated for one gram molecule, must be subtracted.

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* If a precipitate of calcium carbonate is formed through the use of tap water, the reaction is not altered by its presence, since excess of alkali is used, and the turbidity remains; hence no error arises.

For this purpose the calorimeter is filled with an equal quantity of *distilled* water, and the pipette with the same quantity of hydrochloric acid as that used previously; the solutions are mixed as usual. The rise in temperature only amounts to 0·02°—0·03°.

The heat of dilution of hydrochloric acid also includes its heat of dissociation, since when the acid is diluted from 2*n* to 0·08 *n* (corresponding to the use of 20 c.c. of 2*n* HCl and about 500 c.c. of water) the degree of dissociation is increased to a marked extent; this dissociation also develops heat.

What will be the values of the two heats of neutralisation after the corresponding heats of dilution have been subtracted? What does it signify that a smaller value to the extent of about 1000 gram calories is obtained for ammonium hydroxide?

From the ionic equation—

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = Na^{\cdot} + Cl' + H_2O + Q \text{ cal.}$$

it follows that the heat evolution simply represents the heat of dissociation of water, since the equation itself reduces to the form

$$H^{\cdot} + OH' = H_2O + Q \text{ cal.}$$

On the other hand, with the scarcely dissociated NH_4OH, two processes are superimposed, the formation of $NH_4^{\cdot}$ ions, and the disappearance of $H^{\cdot}$ ions; the dissociation of ammonia (corresponding to heat-evolution x, and the accompanying re-formation of water from the ions $H^{\cdot}$ and OH' (corresponding to heat-evolution Q). Since Q is known from the experiment with NaOH, x is equal to the difference of the two heats of neutralisation.

About 14000 gram calories of heat are absorbed by the dissociation of one gram molecule of water; the corresponding figure for ammonia is 1000 gram calories. We have concluded from the heat of dilution of hydrochloric acid that an amount of heat—not accurately measurable from these experiments—is set free when the acid dissociates.

It follows, again according to the principle of Le Chatelier,* that the dissociation of water, which is at a minimum value at ordinary temperature, must increase with rising temperature rapidly, relative to its value, whereas that of ammonia increases much more slowly, and the strong dissociation of hydrochloric acid decreases. This rapid increase in the dissociation of water is shown by the large increase in every hydrolysis accompanying rise of temperature.* A striking example is the behaviour of a solution of ferric acetate when heated; on account of the increase of hydrolysis a quantitative separation of Fe (Cr, Al) from Zn and Mn is rendered possible. Since the dissociation, in other words the *strength*, of ammonia increases much less rapidly than that of water, solutions of ammonium salts (*e.g.*, NH_4Cl) hydrolyse more strongly at higher temperatures, and therefore under such conditions react more strongly acid than at room temperatures.

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* In the form due to van 't Hoff: $\frac{d\ln K}{dT} = \frac{-q}{RT^2}$, where K is the dissociation constant, and q the heat *developed* by the dissociation of a molecule.

5. Heat of Evaporation.

A quantity of the liquid to be evaporated is weighed and introduced into a glass vessel of the form shown (see Fig. 19). The vessel is closed by means of a piece of rubber tubing, through which is inserted a vertical glass tube ending in a capillary and just touching the bottom of the vessel. A suitably bent spiral of narrow copper tubing is fastened to the side tube by means of indiarubber; the spiral is wound round the vessel, and the free end so arranged that it rises to about the same height as the glass tube. The whole can then be immersed conveniently in the calorimeter.

The liquid can be evaporated either by blowing air through the glass tube by means of a small rubber bellows, or applying suction to the end of the copper tube. In either case the air current must only be slight, otherwise the liquid itself may escape through the copper tube, or else the escaping vapour may possess a higher temperature than the bath. It is necessary, in order that the calculation may be simple and straightforward, that the escaping vapour has given up all its free energy. For this purpose the spiral must be long and narrow, so that the bellows or water-pump can only produce a slow effect. If the water pump is used, a small piece of rubber tubing is fixed to the glass tube, and almost closed by means of a clip (as in a vacuum distillation).

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* The extraordinarily high value for the heat of dissociation of water can be estimated at from 13500 to 14000 calories from the abnormal temperature change of the conductivity of the purest water (about 5 per cent. per degree, instead of 2 per cent.), and likewise from the increase of hydrolysis with rise of temperature.

In calculating the water equivalent, only half the amount of the evaporating liquid is taken into consideration, since it escapes during the experiment. Naturally the whole of the copper spiral and glass vessel come into calculation.

Since the experiment lasts several minutes the temperature velocity must be determined with special care; to make it small the work is carried out as far as possible at room temperature. At the close of the experiment the temperature of the calorimeter is measured with an ordinary thermometer.

Exercise.—Measure the heat of evaporation of *ether* by both methods, and calculate the amount per gram (specific heat of evaporation).

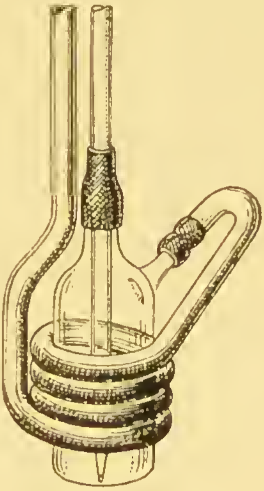

FIG. 19.

Method of Calculation.—The heat of evaporation is composed of two factors, the equivalent of the external work performed in evaporation, and the internal heat of evaporation. If a substance at pressure p expands from volume v_1 to volume v_2 the external work is $p\ (v_2 - v_1)$. In the present case, v_1, the volume of liquid ether, is completely negligible compared with that of the ether vapour, v_2. The external work is therefore pv, where v is the volume of the ether vapour produced at the pressure p. The external work per gram-molecule is PV; the work per gram, consequently, is $\frac{PV}{M} = \frac{RT}{M}$, where M is the molecular weight of ether. Since R in heat units is 1·985 (2 is sufficiently approximate here), the external work is $\frac{2T}{M}$

cal., and this is subtracted from the total specific heat of evaporation.

Remarks.—1. If the heat of evaporation is measured at two widely different temperatures, distinctly different results are obtained; the smaller value corresponds to the higher temperature. All previously measured heat changes are almost independent of temperature. Why?

We can imagine that a reaction takes place at $t_1{}^0$, and that the products of reaction are warmed to $t_2{}^0$, and that in a second experiment the reacting substances are first warmed from $t_1{}^0$ to $t_2{}^0$ and that the reaction then takes place at that temperature. The total heat exchange is equal in both cases. The calculation will show that the difference between the two heats of reaction is equal to the difference of temperature multiplied by the difference of the specific heats of the reacting substances (c_0) and of the products of the reaction (c), and is thus:—

$$Q_{t_1} - Q_{t_2} = (t_2 - t_1)\,(c_0 - c).$$

In cases already studied (solubility, dilution, neutralisation, and precipitation), the specific heat of the system is either completely unaltered by the reaction, or the alteration is inappreciable, because the specific heats of water and of dilute solutions are almost equal. On the other hand, in evaporation and also fusion, the state of aggregation is altered, and the specific heat with it. Since the specific heat of a vapour is smaller than that of the liquid, Q_{t_1} is greater than Q_{t_2} when $t_2 > t_1$. The difference between the specific heats of ether and ether vapour, and the consequent change of the heat of evaporation of ether per degree is about 0·2. At the critical point the heat of evaporation will be zero.

2. It follows qualitatively, from the sign of the heat of evaporation, that the vapour pressure rises with temperature. A quantitative relation can be deduced easily, from these two considerations, between $\frac{dp}{dT}$ and the specific heat of evaporation l:—

$$l = \frac{RT^2}{Mp} \cdot \frac{dp}{dT}.$$

The vapour pressure of ether at 10° is about 289 mm., at 20°

about 437 mm. (for rough reckoning). The mean of the two values is taken for p and T, the difference for dp and dT.

6. Heat of Combustion.

In organic chemistry heats of reaction can only be measured in exceptional cases, since the reactions are slow, and not sharply defined (not ions, but molecules react). The heat changes must in consequence be measured indirectly; accordingly they are deduced from the heats of combustion.

When the substance $C_nH_mO_p$ burns with $(2n + \frac{m}{2} - p)$ O to form $nCO_2 + \frac{m}{2} H_2O$, let the evolution of heat be Q_1. If n gram-molecules of the element carbon, and m gram-molecules of hydrogen are burnt to form carbon dioxide and water the products are also $(nCO_2 + \frac{m}{2} H_2O)$ and the consequent heat evolution Q_2 can be calculated from the tables. The difference $Q_2 - Q_1$ is the heat of formation of the substance.

To bring about complete and instantaneous combustion, the substance is compressed with oxygen into a steel bomb, and the reaction is commenced by a glowing fine iron wire. The heat of combustion is determined in this way at constant volume. (How much greater is the heat at constant pressure when one molecule of $C_nH_mO_p$ is burnt?) The inside of the bomb is protected by a coating of enamel (Fig. 20). The cover is packed with lead, and screws into position, so that the apparatus can stand a pressure of 20—25 atmospheres. The lid contains a valve tube, usually closed by an inserted metal stopper; the end can be screwed on to an oxygen cylinder, and oxygen forced past the valve under pressure. A manometer is inserted between bomb and cylinder. The lid possesses in addition two screw connections. One is directly connected with a metal support inside the vessel, which carries a small crucible or basin, in which the substance is placed. The second is insulated by an enamel partition, and is connected with a second metal rod; the end of the rod when in position is just above the basin. The two metal rods are joined by means of a small piece of thin iron wire, which is heated to redness by a battery of five accumulators. The wire burns, and the falling particles of glowing oxide start the combustion, which is completed in an instant. The substance should be preferably a single piece of solid or in pastilles. The connections should be previously tested by burning several pieces of wire in air, before screwing on the lid. A misfire shows incomplete insulation. The tightness of the apparatus must also be tested. The wire must touch the substance.

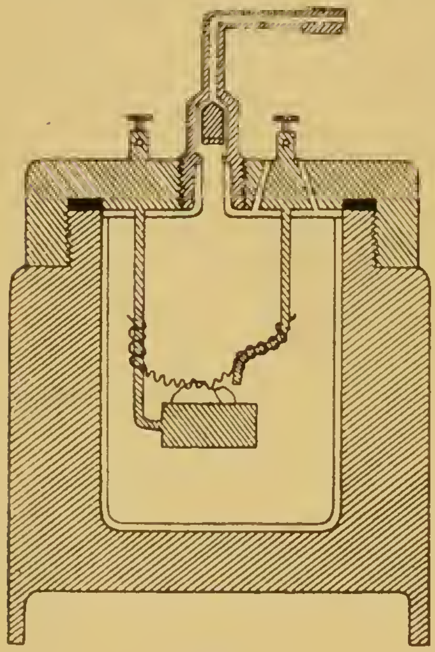
Fig. 20.

The size and weight of the bomb usually employed are too great for the ordinary glass calorimeter beaker. A (ready-made) metal calorimeter of about two litres capacity should be employed; it is placed within a double walled metal vessel, filled with water at room temperature. The very large water equivalent of the bomb makes the calculation uncertain. On this account it is determined specially for the calorimeter and bomb together by burning in the latter a substance whose heat of combustion is known. More exact and elegant is an electrical method of standardisation (see pp. 112 and 125).

Heats of Combustion per gram at Constant Volume.

Cane sugar (mol. wt. 342) . .	3957 g. cal.[*]
Benzoic acid (m. w. 122) . .	6333 ,,
Naphthaleno (mol. wt. 128) . .	9668 ,,
Iron wire	1610 ,,

Exercise.—Standardise the apparatus with naphthalene, and determine the heat of combustion of cane sugar or mannite.

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[*] Why is the heat combustion of one gram of cane sugar so much smaller than that of the same quantity of benzoic acid, and especially of naphthalene?

Enough substance is taken to raise the temperature about one degree. Is it necessary to take into consideration the heat of combustion of the iron wire?

Calculate the heat of formation of the substance measured, on the assumption that the molecular heat of combustion of a gram atom of diamond (C,O_2) = 94300 cal. and that that of a gram molecule of hydrogen is 67520 cal.

ADDITIONAL REMARKS.

Specific Heat of Liquids.

This can be measured more elegantly by electrical methods than by the method of mixtures. Two wires of equal resistance are arranged in series in a circuit with an accumulator and key. Two equal calorimeters are filled, one with water, the other with the liquid whose specific heat is required. One of the wire resistances is immersed in each. The desired specific heat is easily determined from the change of temperature, the amount of liquid, and the water equivalent. If the precaution is observed that the rise in temperature is nearly equal in each case, the temperature velocity can be neglected, and the temperature differences measured directly. If the resistances are not quite equal, they are exchanged, and the measurements repeated.

Specific Heat of Gases.

This is too small to be easily measured by the method of mixture. It is necessary particularly to distinguish between the specific heat at constant volume, c_v, and that at constant pressure, c_p (an unnecessary distinction for solids and liquids of which the expansion is negligible). The difference $c_p - c_v$ is external work corresponding to the expansion; for a gram molecule per degree centigrade it amounts to

$$R = 1{\cdot}985 \text{ cal.} = C_p - C_v.$$

$\frac{c_p}{c_v} = \frac{C_p}{C_v}$ can be deduced from the velocity of sound in the gas under consideration; from this ratio c_p and c_v can be calculated.

Determination of $\frac{c_p}{c_v} = k$.

If u is the velocity of sound

$$u = \sqrt{k \cdot \frac{\text{pressure}}{\text{density}}};$$

for two gases at equal pressure and temperature it follows that

$$\frac{u_1}{u_2} = \sqrt{\frac{k_1}{k_2} \cdot \frac{M_2}{M_1}}$$

where M_1 and M_2 the molecular weights are proportional to the densities of the gases.

If air is chosen as the standard with which comparison is made, $M_2 = 28{\cdot}9$ and $k_2 = 1{\cdot}400$; at 0° the velocity of sound in air is 331 m. per sec., its weight at atmospheric pressure is 0·001293, and the atmospheric pressure in absolute units is 1013200 (see p. 15).* For the same tone the velocity of sound is proportional to the wave lengths l_1 and l_2. The wave length multiplied by the period of vibration is equal to the velocity of sound; the period of vibration for a definite tone is, however, a constant. Hence

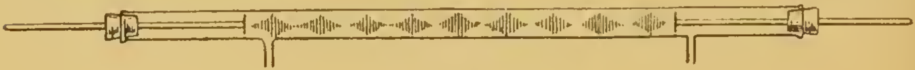

FIG. 21.

$$\frac{c_p}{c_v} = k = 1{\cdot}400 \frac{M}{28{\cdot}9} \frac{l^2_{gas}}{l^2_{air}}.$$

The wave lengths are determined according to Kundt's method. A tube about 1·20 metres in length, and not too narrow, is fitted with side tubes like a Liebig's condenser. Each end is tightly corked and through each cork penetrates a glass rod, carrying at its inner end a cork disk. The corks can be drawn further apart or brought closer by moving the rods, and the effective length of the tube thus altered (see

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* Using abbreviated calculation

$$k = \frac{331^2 \times 10^4 \times 0{\cdot}001293}{101{\cdot}3 \times 10^4} = \frac{329 \times 333{\cdot}3 \times 0{\cdot}001293}{101{\cdot}3}$$

$$= \frac{329 \times 1000 \times 0{\cdot}001293}{3 \times 101{\cdot}3} = \frac{329 \times 1{\cdot}293}{3 \times 101{\cdot}3} = \frac{1{\cdot}097}{1{\cdot}013} \times 1{\cdot}293$$

$$= 1{\cdot}293 \times 1{\cdot}084 = 1{\cdot}3 \times 1{\cdot}078 = 1{\cdot}401.$$

With some exercise in abbreviated methods the calculation can be shortened still further.

Fig. 21). The tube is powdered uniformly with lycopodium or dry fine sand, or cork powder. The glass rod is rubbed with a damp duster, which produces longitudinal vibrations; in this way vibrations are set up in the air or gas in the tube. These are reflected from cork to cork and become stationary waves. The half-wave lengths are distinctly shown by means of the powder which gathers at the nodes. The length between the two discs should be adjusted to give the best effect.

Exercise.—Determine $\frac{c_p}{c_v}$ for carbon dioxide. Measure first l for air, then displace the air through the side tubes by gas from a small Kipp's apparatus. The method of determining the average result has been indicated on p. 4. Calculate c_p and c_v.

Remark.—According to the Kinetic theory of gases $\frac{c_p}{c_v}$ is $\frac{5}{3}$ for an ideal gas. This figure has actually been found for monatomic mercury vapour and for argon, helium, etc. For diatomic gases the average value is about 1·4, for triatomic gases 1·3. As the number of atoms in the molecule increases, the value approaches unity asymptotically. By analogy, the argon gases are monatomic, since $\frac{c_p}{c_v}$ has the theoretical value; this is confirmed by their chemical indifference, and by the fact that their atomic weights, calculated on this assumption, allow them to occupy probable positions in the periodic system.

CHAPTER V

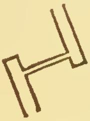
THE DETERMINATION OF OPTICAL CONSTANTS

OPTICAL constants are pre-eminently suitable for the characterisation and identification of liquids and dissolved substances, for the investigation of their constitution and for the analysis of solutions and mixtures.

While the *refractive index* can be measured for all substances (refractometry), *light absorption* is only measured in the case of coloured substances, and the *rotation of the plane of polarisation* for optically active bodies (polarimetry).

It must be remembered particularly in all optical determinations, that examination in only one kind of monochromatic light has no scientific value; sodium light, specially favoured by chemists on grounds of convenience, is insufficient in most cases. Measurements of refractive index and of rotation must be carried out at a definite temperature; in most cases an exact determination of density is also necessary.

Source of Light.

Common salt, freed from mother liquor by heating, or a mixture of finely powdered common salt and sodium bromide, is introduced into the flame of a bunsen burner on a piece of platinum wire, or a ring-formed platinum spoon; the resulting light is bright enough for most purposes. Soda or borax is less bright, but less inconvenient on account of its slighter volatility. An absolutely homogeneous light is obtained if necessary by filling a double glass trough with potassium bichromate and uranium sulphate solutions and placing it between the source of light and the apparatus. In lengthy experiments the sodium chloride-bromide flame must be placed under a draught hood, since the bromide vapour attacks both apparatus and organs of respiration. A very bright light is obtained by completely saturating a small roll of nickel wire-gauze with the melted mixture of NaCl—NaBr, and suspending it over a powerful burner by a stout nickel wire. The salts can be fused in a blow-pipe. If hydrogen tubes are to be employed, the  form, which can be used lengthways, is most convenient. A small or medium-sized induction coil and two accumulators suffice for transparent solutions.

Lithium and thallium light are seldom used. Sodium and hydrogen light give spectrum lines arranged over the visible spectrum with sufficient symmetry.

The lines in question which are recommended are

$H_\alpha = C =$ red (656·3 $\mu\mu$),
Na $= D =$ yellow (589·3 $\mu\mu$),*
$H_\beta = F =$ green-blue (486·1 $\mu\mu$),
$H_\gamma = G =$ blue-violet (434·1 $\mu\mu$).

Refractometry.

Modern apparatus makers, especially Zeiss in Jena, have supplied the chemist with an instrument far more convenient in working than the formerly exclusively-used *spectrometer*. This, when employed for exact measurements, requires frequent centering and adjustment. Every measurement of a refractive index necessitates a measurement of the angle of refraction of the prism and a determination of the deviation of the rays; in addition the latter must be measured by the method of minimum-deviation for each wave length. Again, when liquids are under examination, it is necessary to use prisms with exactly parallel sides. With the modern forms of apparatus these inconveniences in great part disappear.

Consequently in this work reference is made only to modern instruments which depend on an inversion of the principle of *total reflection*.

If a 90° pencil of light rays passes from air into a liquid whose coefficient of refraction is n, the pencil is bent together to a smaller angle α; the value of α can be calculated easily from Snellius' law of refraction:

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* D, strictly speaking, comprises two lines, D_1 and D_2, with the respective wave lengths 589·6 and 589·0 $\mu\mu$.

$$\frac{\sin 90^\circ}{\sin \alpha} = n; \qquad \sin \alpha = \frac{1}{n}.$$

Hence an eye placed at A (Fig. 22) in the liquid would observe a sharp division between the light and dark regions. If α can be measured, n can be calculated from the equation.

The most convenient instruments, based on this, the inverted principle of total reflection, are:

1. *Pulfrich's Total Reflectometer.*
2. *Zeiss' Immersion Refractometer.*

In the first instrument (Figs. 23 and 24), a ground glass cylinder is cemented to a strongly refracting right-angled prism; a few drops of the liquid which is to be investigated are transferred to the cylinder with a pipette. A great advantage of the apparatus is that only just enough liquid is required to cover the bottom of the cylinder. However, in practice enough is used to cover the bulb of the thermometer completely (Fig. 23*b*), so that the temperature can be measured accurately. With very volatile liquids the thermometer is fixed through a tight-fitting cork.

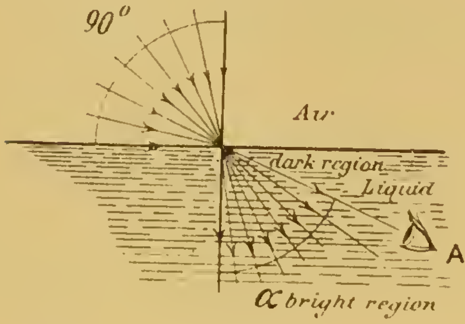


FIG. 22.

The boundary surface liquid-prism must be illuminated by incident rays of homogeneous light. Sodium light is used most often, concentrated through a lens (not shown in the illustration) from a rigidly-fixed apparatus, on to the upper face of the prism. If the light is correctly focussed a sheet of paper held at the cemented junction of cylinder and prism will show a sharp (inverted) image of the flame. Light entering through the calibrated part of the circle S (Fig. 24) emerges from the vertical face of the prism at an angle α to the horizontal, which is measured. For convenience the telescope T is turned at half right-angles towards the front. The arm carrying the telescope is provided at the other extremity with a vernier *V* by which minutes can be read; as seen through the telescope, a somewhat curved bright-dark boundary line must touch the middle point of the cross wires if the adjustment is sharp (Fig. 25). The first approximate adjustment is made with the hand. After this has been done, the screw *F* is tightened; this prevents further movement of the telescope, and the final adjustment is made by cautiously turning the micrometer screw *M*.

Calculation.—Let the refractive index of the large prism compared with air be *N*, the unknown index of the liquid compared with air be *n*, the observed angle, *a*, and the angle (not measured) which the ray entering the prism makes with the perpendicular to the prism be β. Then $\frac{N}{n} = \frac{1}{\sin\beta}$; $n = N \sin\beta$; moreover, for the emergence of the rays into air $\frac{\sin a}{\cos\beta} = N$; $\cos\beta = \frac{\sin a}{N}$; $\sin\beta = \sqrt{1 - \frac{\sin^2 a}{N^2}}$; and therefore $n = \sqrt{N^2 - \sin^2 a}$. *N* varies but slightly with temperature. A table is supplied with the instrument, which gives n_D directly as a function of *a* and contains the necessary correction for other than sodium light. N_D for the prism is generally between 1·61 and 1·62. For a few liquids which are very strongly refractive, such as carbon disulphide, and some bromine and iodine organic compounds, the usual prism is

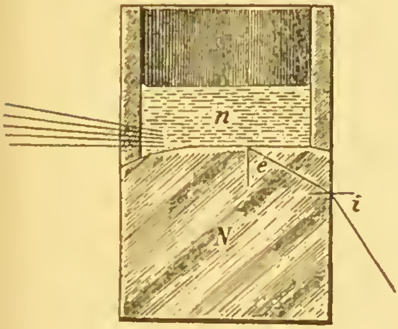


FIG. 23*a*.

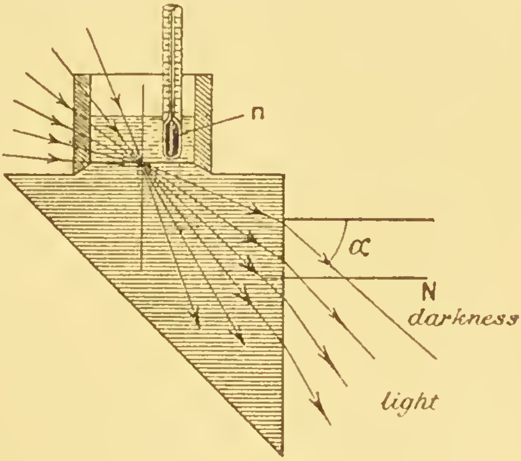


FIG. 23*b*.

insufficient. For the hypothesis of the method is that $n_D < N_D$. If the dispersion of liquid and prism are equal, the light rays are not separated from one another by the use of a non-homogeneous light, *e.g.*, hydrogen light; if the dispersion of the liquid is greater than that of the prism, which happens occasionally, the spectrum is seen in inverted order: violet, blue, yellow, red. The calculation is unaltered. If two light rays coincide, so that an accurate reading is impossible, a slightly different temperature is employed. Since the dispersion of glass is almost unaltered by temperature, while that of the liquid sinks as temperature rises, the images will separate from one another at higher or lower temperatures, of course in reverse directions.

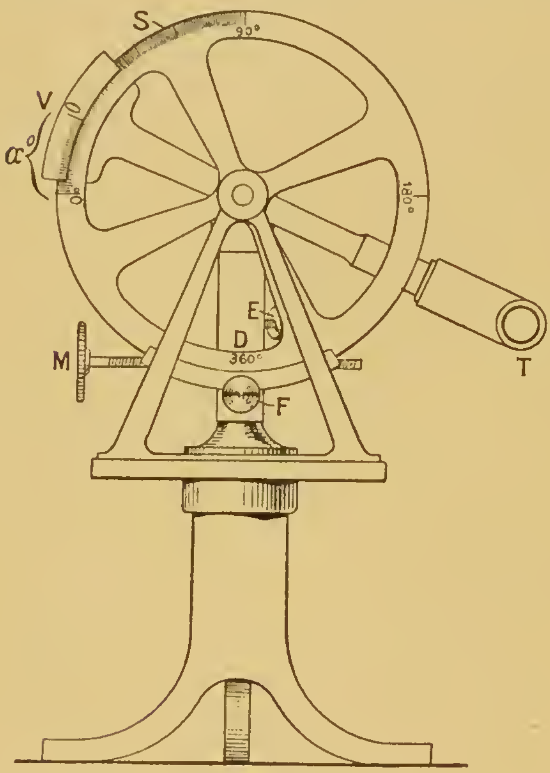


FIG. 24.

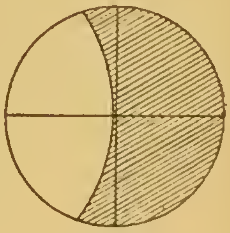


FIG. 25.

Practical Remarks.

The glass prism is very sensitive, both chemically and mechanically. After washing, it must only be dried with old soft linen, or soft chamois leather. The place in the prism and cylinder through which light enters the liquid must be kept particularly clean. Moreover, special attention must be paid to the cementing of the cylinder (by means of fish glue, gum arabic, water glass, or canada balsam, according to the nature of the liquid under investigation).

The bottom of the cylinder must lie in the centre of the circle. This is the case when the three prism edges (*D*) are perpendicular to the ground-plate of the instrument, and the side screw (*E*) is tight.

The eye piece of the telescope, and the lens of the vernier (not shown in the figure) must be correctly focussed.*

When a lamp burns in the room, a possible source of error arises from light falling from above on to the glass cylinder. This is therefore protected by a cover.

Exercises.—1. The apparatus is tested by a measurement of the index of refraction of distilled water for sodium light. For water at temperature t

$$N^t_{\mathrm{D}} = 1{\cdot}33381 - 0{\cdot}00000125t - 0{\cdot}000002t^2$$

$$= 1{\cdot}33381 - \frac{t}{800000} - \frac{t^2}{500000}.$$

The corresponding value for n and the theoretical angle a are calculated, making the necessary correction for the observed temperature; $sin\ a = \sqrt{N^2 - n^2}$. The difference between the observed and calculated values of a is applied as a correction to all fresh measurements. It is thereby assumed that the calibration of the apparatus is correct in itself, but makes a constant error with the horizontal amounting to $a_{obs.} - a_{calc.}$

2. Determine the index of refraction of benzene and chloroform at two temperatures, and calculate the value of the *molecular refraction*, independent of temperature,

$$= \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2} \text{ (see below).}$$

---

* All adjustments are simplified by the following device: With instruments which have been in use in the laboratory for a considerable time, the highly polished metal of the telescope adjustment becomes tarnished where it is not protected by the outer case. By arranging that the boundary between dull and polished surface coincides with the end of the outer case, it is only necessary to make a slight adjustment according to the peculiarity of the eye.

If the coefficient of refraction is measured correctly to 0·0002, which is not difficult if care is taken, then the uncertainty of $\frac{n^2 - 1}{n^2 + 2}$ is about 0·03 per cent., and consequently d must be known to three units in the fourth decimal place. However, most of the laboratory preparations contain more than 0·03 per cent. of impurity.

Hence to calculate d the following data suffice :—

$$\left.\begin{array}{l}\text{Benzene } d^{20}/_4\ 0{\cdot}880\,; \\ \text{Chloroform } d^{20}/_4\ 1{\cdot}489\,;\end{array}\right\}\ \text{Coefficient of cubical expansion} = 1/800.$$

Molecular Refraction and Dispersion.

Let M signify the molecular weight, N the index of refraction for infinitely long waves; it can be shown theoretically that there exists for every substance a characteristic constant $\frac{M}{d} \cdot \frac{N^2 - 1}{N^2 + 2} = R'$, which is independent of temperature, pressure, and state of aggregation, and which is termed its *molecular refraction*. Here the volume actually obtained from one gram molecule is taken, whilst $\frac{M}{d}$ gives the total volume of the molecule plus the ether envelope.

If N is replaced by the refractive index n, for a selected kind of light, a remarkable constancy is obtained.

The molecular refraction can be divided into parts, each part representing the equivalent refraction of a single atom in the molecule: *e.g.*, C + H + 3 Cl = $CHCl_3$. Nevertheless the molecular refraction is not a purely additive magnitude, but depends to a high degree on constitution, which is especially noticeable with atoms of the same valency.

To each kind of linking corresponds its own refraction equivalent. In the case of organic compounds, the molecular refraction is not merely the sum of the atomic refractions, but in addition equivalents for the double and triple carbon linkings (written $\vDash$ and $|\!\!\equiv$) must be taken into account. The rise is small for ring compounds, so that the molecular refraction of benzene is the sum of 6 C + 6 H + 3 $\vDash$. It is evident that the measurement of molecular refraction offers a remarkable expedient for the investigation of constitution. The values found for benzene and chloroform should be compared with those calculated from the following table:—

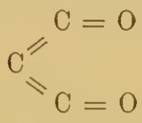
Atomic Refraction.	r_α	r_D	r_γ	$r_\gamma - r_\alpha$
Singly linked carbon atom $-\overset{\vert}{\underset{\vert}{C}}-$	2·365	2·501	2·404	0·039
Hydrogen H—	1·103	1·051	1·139	0·036
Chlorine Cl—	6·014	5·998	6·190	0·176
Bromine Br—	8·863	8·927	9·211	0·348
Iodine I—	13·808	14·12	14·582	0·774
⊨ ... $C=C$	1·836	1·707	2·07	0·23
⊫ ... $C\equiv C$	2·27	2·10	2·49	0·22
Hydroxyl oxygen $O-H$	1·506	1·521	1·525	0·019
Ether oxygen $O <$	1·655	1·683	1·667	0·012
Carbonyl oxygen $O =$	2·328	2·287	2·414	0·086

It also follows from the table that since $r_\gamma - r_\alpha$ is especially large for the carbon linkings (⊨ and ⊫), hydrogen light must be used whenever possible, in the investigation of constitution. The dispersion values $r_\gamma - r_\alpha$ are not quite so constant for ⊨ and ⊫ as the atomic dispersions, so that only two decimal places are given above. The values for r_D are deduced by another principle than those for r_α and r_γ and are not comparable with them. Sometimes they are larger than r_α and r_γ, sometimes smaller. A calculation of $r_D - r_\alpha$ or $r_\gamma - r_D$ from the above table has, in consequence, no value.

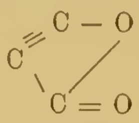
The values in the table are the results of a calculation by adjustment. By the method of least squares or some similar method the additive constants are found which will give with the minimum error the accurately determined molecular refractions of a few chemically pure substances. These values are tested for a very large number of new observations, and it is proved that the numbers calculated for a limited number are valid for all.

Slight differences of constitution still affect the value, and these must be taken into consideration. Thus the value depends not only on the number but also the reciprocal position of the double linkings.

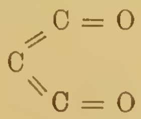
Example.—Two formulæ are ascribed to carbon suboxide C_2O_3—



and



According to the first formula M_D should equal 15·49 and $r_\gamma - r_a$, 0·75; for the second $M_D = 13·57$, $r_\gamma - r_a = 0·44$. The observed values are $M_D = 16·6$, $r_\gamma - r_a = 0·8$ approximately, values somewhat higher than those calculated from the first formula. Such an excess is often observed with a number of double linkings. With heterocyclic unsaturated ring systems, on the other hand, there generally is found a "depression," *i.e.*, a value smaller than that calculated from the above table. Hence the conclusion is reached that the constitutional formula of carbon suboxide is



If instead of a homogeneous liquid a mixture (a solution) is used, then the total refraction is approximately the sum of the specific refractions of the constituents. If a solution of specific gravity d contains p per cent. of dissolved substance, and its refractive index is n, while the solvent has the corresponding values d_0 and n_0, the specific refraction of the dissolved substance is equal to

$$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}\cdot\frac{100}{p} - \frac{n_0^2-1}{n_0^2+2}\cdot\frac{1}{d_0}\cdot\frac{100-p}{p}.$$

The molecular refraction is obtained by multiplying by the molecular weight. The method, as a difference method, is very susceptible to experimental error, and is not free from objections theoretically.

Pulfrich's Refractometer can also be used to determine the refractive index of solids, whether amorphous or crystalline (except monoclinic or triclinic crystals). They are suspended in a liquid as fine powders. If the mixture is non-homogeneous optically, no sharp bright-dark boundary line is obtained. By mixing together an optically stronger and an optically weaker solution, a mixture is obtained which has the same refractive index as the solid; an optically homogeneous substance results which gives as sharp a boundary line as a mechanically homogeneous substance. A similar principle is employed to determine the density of solids (see p. 35), and can also be used to determine their dielectric constant ("Optical Suspension Method").*

Exercise.—Determine the refractive index of potash alum, $KAl(SO_4)_2, 12H_2O$, in a mixture of chloroform and benzene. Shake a quantity of salt which can be taken up on the blade of a penknife into the cylinder containing chloroform from the last experiment ($n = 1{\cdot}44$ to $1{\cdot}45$). Add benzene ($n = 1{\cdot}50$) drop by drop from a pipette. The field of vision gradually brightens; the boundary line becomes sharper. If too much benzene is added, a brighter band appears at the boundary, since total refraction occurs in the system optically weak powder—optically strong liquid. When a sharp boundary is obtained, the reading gives the coefficient of refraction of the alum—after taking into consideration the correction ascertained by means of water—according to the previous method of calculation employed for pure liquids.

Zeiss's Immersion Refractometer.

If the concentration of a solution is to be deduced from its refractive index (refractometric analysis), Zeiss's immersion refractometer is used for aqueous and alcoholic solutions, and is standardised by a series of measurements.

The principle is the same as that for Pulfrich's instrument, but the prism (angle of refraction about 63°, $n_D = 1{\cdot}51$) and the reading apparatus are mounted on the same axis. The bright-dark boundary is shown on a finely divided scale, *Sc*, with arbitrary divisions, on which the powerful lens *Oc* is sharply focussed. The limits of the scale, -5 and $+105$, correspond to the indices 1·32539 and 1·36640. Daylight or lamplight is used for illumination, and rendered achromatic by passage through an Amici-prism *A* (Fig. 26) fixed inside the apparatus; this is adjusted by means of the screw-ring *R*, situated midway in the height of the instrument. For every liquid or solution the instrument must be achromatised afresh. The screw ring is graduated, and provided with a fixed pointer. The indices — measured in arbitrary units — are proportional approximately to the amount of dispersion. With the apparatus is sold a water bath with openings for ten small glass beakers, each of about 80 c.c. capacity. By means of the hook *H* (Fig. 26) the refractometer is hung on the ⊓-shaped metal stand above the water bath, so that the prism *P* is immersed in a glass beaker. The prism face is illuminated by means of an inclined mirror placed beneath the water bath.

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* The refractive index of a solid varies very little with temperature, but that of a liquid greatly (corresponding to the alteration of volume), so that the liquid-solid system again becomes non-homogeneous for every change of temperature.

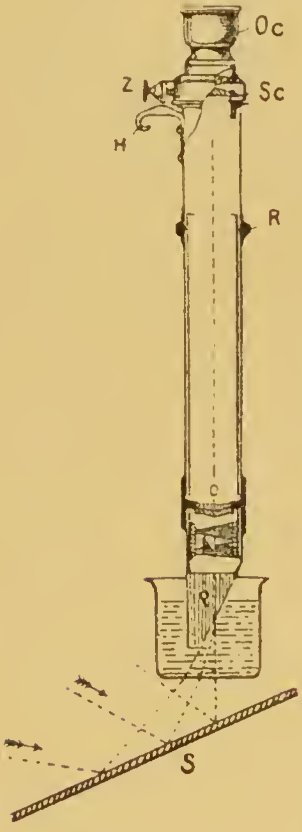


FIG. 26.

The internal arrangement of the apparatus is shown schematically in the figure, which also illustrates the passage of light rays. The water bath is not shown ; it serves merely to regulate the temperature.

The scale *Sc* is so arranged that the boundary line stands at 15·0 when the prism is immersed in distilled water at 17·5°. The micrometer screw *Z* is furnished with two bosses, and allows the scale to move over a whole division; in this way the position of the boundary line can be accurately read. The barrel of the screw is divided into ten parts, so that the hundredth part of a scale division can be estimated. At the commencement of a measurement the screw is set at zero. If the boundary line does not lie on a scale division, the screw is turned until the boundary line and the nearest scale division coincide ; the screw reading is added to the scale reading. With good illumination and a little experience the error of reading is only 0·03 of a scale division.

The apparatus is standardised with the salt to be examined, by employing solutions at three concentrations, preferably in the ratio 0 (water) : 1 : 2 : 4. In each case 50 c.c. are used.

The bath is filled with tap water at 17·5°, or when the room temperature is considerably different from 17·5°, a stream of water is allowed to flow from a large supply at 17·5°. Four beakers containing the solutions are arranged in the bath, and when the bath temperature is attained the refractometer is hung in the small beaker containing water, and a reading taken; this should be 15·00. The prism is then dried with a fine linen cloth and placed in the next most dilute solution, and so on. Finally the measurements are repeated in the inverse order, and the mean of each pair of readings taken. If the temperature of the bath alters slowly and regularly, by this method all the readings will be made at the same average temperature; the deviation of temperature from 17·5° will have no appreciable effect, since the temperature coefficients of water and solution are the same for small differences of temperature. A table is provided with the apparatus by which the scale reading can be converted into the refractive indices for sodium light. This calculation is superfluous when only analytical results are sought.

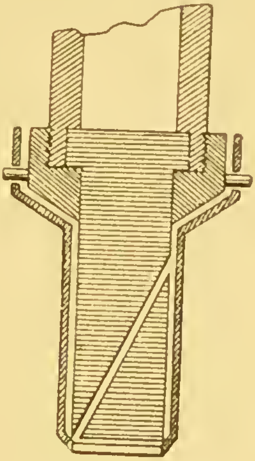


FIG. 27.

On the contrary the relation between concentration c and displacement of the boundary line compared with water is expressed directly in scale units. Let this displacement be Δ.

A quadratic equation is always sufficient to express c as a function of Δ (or Δ as a function of c): $c = \alpha \Delta + \beta \Delta^2$.

β is usually small, so that a linear equation often suffices as a first approximation. If α and β are calculated from the two most concentrated solutions, the formula can be tested by application to the third solution, and the apparatus is in this way standardised for the substance in question.

The apparatus is very suitable for testing solutions employed for titrations, which should of course contain no chemically indifferent foreign substance.

Exercise.—Standardise the apparatus with a salt which can easily be procured (such as $NaCl$, KCl, Na_2SO_4, or $BaCl_2$), and then analyse a solution of unknown strength.

At the conclusion of the measurements transfer the instrument without wiping the prism from water to the most concentrated solution. The reading is indistinct through the current streams produced, which illustrates convincingly the sensitiveness of the apparatus.

Remark.—The complete apparatus is provided with a second, separate, wedge-shaped prism, fitted into a holder, and fastened to the prism by a bayonet clasp (Fig. 27). This device permits accurate measurements of small amounts of liquid. The instrument, with the second prism suspended, is immersed in the liquid bath. It is then similar to an Abbé's refractometer, but with a smaller range.

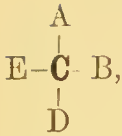
Polarimetry.

General Remarks.

Ordinary light consists of ether waves vibrating in three directions; when such light passes through a prism of Iceland spar, two rays of light emerge (hence the name "doubly refracting spar"); these vibrate in two planes which are at right angles to each other. The light of each ray vibrates in one plane only, and is said to be *polarised* or *plane-polarised.* If a crystal of Iceland spar is cut in a particular manner, and the two sections cemented together by a thin layer of Canada balsam, only one of the rays of light can emerge; the other is totally reflected at the boundary between crystal and balsam. Hence with such a prism, known as a *Nicol*, ordinary light is broken up into two components, of which one disappears, and the second emerges completely polarised.

When this light passes through a second prism of the same size, there is no alteration of the light intensity, if the two prisms are in precisely similar positions. If, however, the second is rotated round its axis, the intensity of the emerging light varies with the extent of rotation, becoming zero when the angle of rotation is 90°, *i.e.*, when the plane of the first Nicol (*polariser*) is at right angles to that of the second (*analyser*).

All substances which contain an asymmetric carbon atom,



$$\begin{array}{c} A \\ | \\ E-\mathbf{C}-B \\ | \\ D \end{array}$$

rotate the plane of polarised light, provided they are not mixtures of two substances, rotating in opposite directions to an equal degree.

Consequently when the planes of two prisms are at right angles so that all the light is cut off, and such a substance, if a liquid, or its solution, if a solid (an *optically active* liquid or solution), is placed between them, the plane of polarisation is rotated as it passes through the solution, so that the second prism no longer cuts off all the light. To restore the condition of absolute darkness the analyser must be rotated through a certain definite angle. This is always less than 90°, but may be either to right or to left (clockwise or counter-clockwise). In the former case the solution is termed *dextro-rotatory;* if a rotation to the left is necessary, *lævo-rotatory.*

The rotation angle a depends on both the nature and length of liquid, and also on the wave length of the light employed and the temperature of measurement. Since the length of the liquid alters the angle of rotation, where solutions are used with inactive solvent, the angle will be, for a similar reason, proportional to the concentration. This permits the use of polarimetric measurements to determine the concentration of solutions, or, if that is known, the purity of the solute.

The most important and well-known *active* substance is cane sugar; a special apparatus has been constructed for its examination and estimation. The rotation produced by the sugar is counterbalanced by the rotation of a movable quartz plate in the opposite direction. Since this apparatus, the *saccharimeter*, can only be used for cane sugar, it is not taken into consideration here.

An apparatus is suitable for accurate scientific measurements only when the rotation produced by the active substance is compensated by the measured rotation of a calc-spar prism (generally a Nicol's prism). The simplest type of instrument consists merely of a fixed polariser, the substance under examination, and the analyser; the two prisms consist of a fixed and a rotating Nicol. The accuracy of measurement is improved by slightly deflecting the direction of polarisation of part of the light. This is done most preferably, as in Lippich's type of instrument, by the insertion of a small

Nicol[*] between the polariser and the substance; this is rotated slightly so that its axis makes a small angle δ with that of the polariser.

With this arrangement, for no position of the analyser is the whole field of vision completely dark, or completely bright. *E.g.*, if the axes, and consequently the directions of oscillation of analyser and polariser, are at right angles to each other, then one half of the field of vision will be absolutely dark. However, of the light rays polarised in a slightly different direction by the small Nicol, a part proportional to $\sin^2 \delta$ will penetrate the analyser[†] (see Fig. 28, position I.).

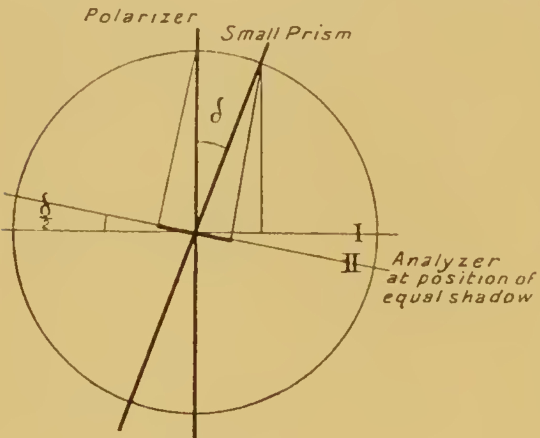


Fig. 28.

The two parts of the field of vision are equally illuminated by penetrating light rays at four positions of the analyser; these differ by steps of 90°. These are when the oscillation directions of the two large Nicols enclose the angles

$$\frac{\delta}{2},\ 90^\circ + \frac{\delta}{2},\ 180^\circ + \frac{\delta}{2},\ \text{and } 270^\circ + \frac{\delta}{2}.[‡]$$

Only two positions (differing by 180°) are actually used for measurements, namely, those at which very *little* light penetrates (angles $90^\circ + \frac{\delta}{2}$, and $270^\circ + \frac{\delta}{2}$ respectively;

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[*] In cheaper forms of instrument (Laurent's half-shadow apparatus) this effect is produced by the insertion of a semi-circular quartz plate of definite thickness, which covers half the field of vision. The thickness of the plate must be such that the phase of transmitted sodium light is altered by a half-wave length. Such an apparatus consequently can only be used for *one* kind of light; even for this it is less trustworthy than Lippich's form.

[†] The amplitude of the penetrating rays is proportional to $\sin \delta$, and, therefore, the intensity to $\sin^2 \delta$.

[‡] It is here presumed, though not strictly correctly, that the light intensities in both halves of the field of vision are equal. In reality the small Nicol absorbs and reflects a little light.

position II. in the figure; **position of equal-shadow**). The illumination of the two halves of the field of vision is proportional to $\sin^2 \frac{\delta}{2}$.

In these positions very little rotation is necessary to make either the one or the other half of the field of vision quite dark. And since this depends on the value of δ, the smaller δ is taken, the smaller will this rotation become. But at the same time the total illumination is decreased, and the position of equal shadow is much more difficult to determine. Hence to perceive such small differences the source of light must be as intense as possible (but strictly homogeneous). Consequently the accuracy of measurement increases the smaller the angle δ, and the greater the light intensity.

A more accurate instrument contains *two* equal small Nicols (instead of *one*) placed next to the polariser, so that a comparison field is obtained on each side of the unscreened portion (*third-shadow apparatus*).

The position of equal shadow is obtained in the following manner: the analyser is always provided with a lever, or a toothed-wheel movement; it is by that means rotated quickly backwards and forwards about a smaller and smaller angle on either side of the exact position. In this way a vertical shadow appears to pass across the field of vision. The position is taken where the shadow seems to pass the dividing line of the two halves; it is necessary to take care, however, that it is approached alternately from one side and then the other. With a somewhat steady hand guidance by means of a single lever completely suffices, and the costly toothed-wheel movement is unnecessary. If a tube, with liquid or solution which is to be examined, is placed between analyser and polariser, the former must be rotated through some angle (a) from its first position, and adjusted in the same way for equal shadow of the whole field of vision. This angle a is measured. Equal darkness is only attained with perfectly homogeneous light.

As has been stated, the size of the angle a depends on the particular rotation of the active substance, its density (d), the thickness of layer through which the light passes (l), the temperature (t) and the wave-length of the light employed;

moreover, in the case of solutions, it depends on the concentration of the solution, on the solvent, and occasionally also on impurities in the solution. If the **specific rotation** $[\alpha]$ is calculated, the measurement is rendered independent of several of the variables ; $[\alpha]$ is defined as the rotation which results when one cubic centimetre of liquid contains one gram of active substance, and the rays of light pass through a column of this liquid 10 centimetres in length. If sodium light is employed, and the temperature of measurement is t°, then for homogeneous liquids,

$$[\alpha]_D^t = \frac{\alpha}{l \cdot d},$$

where l is measured in decimetres. In the case of a solution containing p per cent. of active substance by weight, its concentration c, the number of grams per 100 c.c. of solution, is equal to pd, and

$$[\alpha]_D^t = \frac{100\ \alpha}{l \cdot c} \text{ or } \frac{100\ \alpha}{l \cdot p \cdot d}.$$

If $[\alpha]_D^t$ is known, p or c can be calculated from a measurement of the angle α (polarimetric analysis).

For cane sugar the specific rotation for sodium light $[\alpha]_D$ is almost independent of both temperature and concentration. A rise of temperature of 1° lowers $[\alpha]$ by about $\frac{1}{1000}$ only. The relation for solutions containing up to about 25 per cent. of cane sugar can be represented by the shortened formula $[\alpha]_D^{20} = 66{\cdot}39^\circ + 0{\cdot}015\ p - 0{\cdot}0004\ p^2$. If $[\alpha]_D^{20} = 66{\cdot}5^\circ$ is the value taken, the error for a from 5 to 25 per cent. solution is less than 0·2 per cent. of the value, and is in consequence less than the error of experiment. The formula is obtained :—

$$c = \frac{100\ \alpha}{66{\cdot}5\ l} = \frac{1{\cdot}504\ \alpha}{l};$$

if the tube of usual length (2 decimetres) is used, $c = 0{\cdot}752\ \alpha$. If p is to be calculated, we can write at 20°

$$d = 0{\cdot}9983 + 0{\cdot}00289\ \alpha,$$

so that

$$p = \frac{0{\cdot}752\ \alpha}{0{\cdot}9983 + 0{\cdot}00289\ \alpha},$$

and so finally, for small values of a (up to about $a = 15°$)

$$p = 0{\cdot}752\, a\, (1{\cdot}0017 - 0{\cdot}0028\, a).$$

As counterpart to cane sugar a mixture of glucose and fructose can be employed, arising from the action of acids on cane sugar. In this case $[a]$ varies considerably both for concentration and temperature. The following formulæ have been deduced :—

$$[a]_D^{20} = -19{\cdot}66° - 0{\cdot}036\, c \text{ and } [a]_D^{20} = -19{\cdot}63° - 0{\cdot}05\, p.$$

Between 0° and 30°

$$[a]_D^t = [a]_D^{20} + 0{\cdot}304\,(t - 20) + \frac{(t - 20)^2}{600}.$$

Here the values of $[a]$ are calculated absolutely. The lævo-rotation decreases with rise of temperature.

A temperature measurement is therefore necessary for invert sugar. $[a]_D$ alters per degree rather more than 1·5 per cent. Larger tables of values are found in Landolt's book, *Die optische Drehungsvermögen*, 2nd edit., Brunswick, 1898, and also in Landolt-Börnstein.

Special Directions for Measurement.

The liquid is contained in a tube of definite length (in most cases 20 cm.). The ends are ground, and a screw thread of brass is cemented externally to each. They are closed by plates of glass with parallel sides, which are screwed on by means of a brass cap; a rubber ring acts as protection and renders the tubes liquid-tight. The ends must not be screwed on so tightly that the glass plates become strained, since under great pressure glass becomes doubly refracting and an exact measurement is rendered impossible. No air bubbles must be permitted between the plates. The most suitable form is that shown in Fig. 29. The funnel-shaped orifice allows the tube to be filled, and emptied. A thermometer can also be inserted in it.

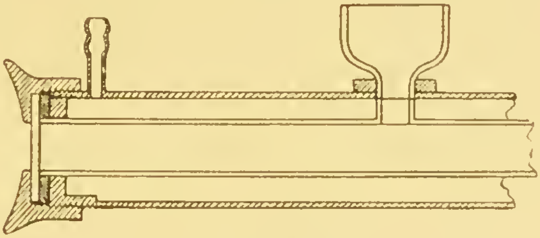

FIG. 29.

For accurate measurements at a definite constant temperature, the glass vessel is surrounded by a metal jacket resembling a Liebig's condenser. Water at constant temperature passes through the jacket from a cistern or thermostat.

After a measurement is completed the solution is immediately poured out, and the caps unscrewed. Tube, caps, glass plates, and small rubber disks are washed with distilled water and dried.

Every apparatus contains, besides the tube and its fittings, a system of lenses and prisms which is shown schematically in Fig. 30.

Light from the lamp, or source of light, *L** passes through a circular opening *B*, a lens *L′*, the polariser *P*, in part through the adjacent small Nicols, and then through a second opening *B′*; thence it passes through the measuring tube *R*, or through the corresponding air space. The lens *L* projects an image of the lamp through a third opening *B″*, behind which is the rotating analyser, firmly connected to two verniers, as well as a small telescope *T*. The scale *S*, over which the verniers move, remains fixed. The telescope is focussed accurately on the slit *B′*, so that at positions of different brightness the parts of the field of vision are separated by division lines, as though they had been drawn with a pen. Since the solution must refract light more strongly than air, the eye-piece is focussed quite independently in the two cases.

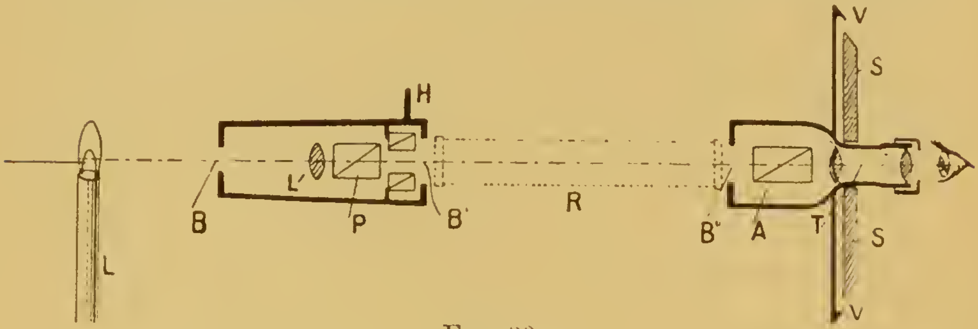

FIG. 30.

H is a handle by the rotation of which the angle δ (see p. 84) between the oscillation directions of the polariser and the small Nicol (or Nicols) can be altered. This is never done *during* a measurement. With a turbid or coloured solution δ must be made large for both the zero-point determination and the actual measurement, since otherwise the intensity of the light is reduced to such an extent that the measurement is inexact, and the eye is strained. Each displacement of δ alters the position of equal shadow of the apparatus, which, as a matter of fact, deviates $\frac{\delta}{2}$ from the true zero position, where the planes of the analyser and polariser are at right angles to one another.

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* The light should be passed through a solution of potassium bichromate (see p. 70).

In exact determinations, the zero-point of the apparatus should be measured before and after the measurement with the solution.

If possible the work should be carried out in a dark room; in order to take the reading a small pocket electric lamp is convenient.

Exercise.—Prepare a 15—20 per cent. solution of very pure cane sugar (weighing to 0·1 per cent.). Examine this in Na-light at 20°, and calculate the sugar-content by weight or by volume (in whichever way the solution has been made up).

If there is ground for suspicion that the solution contains a second active substance, besides cane sugar, polarimetric analysis can be applied to the mixture. The second value, necessary for the determination of two unknown quantities, is obtained by measuring the rotation after the cane sugar has been converted into invert sugar by heating it with a few cubic centimetres of concentrated hydrochloric acid. At 20° $[a]_D$ is $+$ 66·5° for an approximately 15 per cent. solution before inversion; afterwards it is $-$ 20·4 to $-$ 20·5° (see p. 86). Per decimetre thickness of layer, and per 1 per cent. cane sugar, the rotation changes 0·870°. From the actual change observed the cane sugar content is calculated, and the corresponding rotation subtracted from the actual initial rotation. The excess corresponds to the rotation of the impurity. If in inverting the sugar the solution is diluted, as by the addition of 10 c.c. HCl to 100 c.c. solution, heating, cooling to 20°, and again making up the total volume to 110 c.c.; the dilution must be taken into consideration in making the calculation, in this case by multiplying the angle of rotation by 1·1.

Exercise.—Take a grape-sugar solution of known strength and determine its specific rotation; add 1 c.c. to 50 c.c. of the sugar solution already employed, and calculate the rotation of the addition by the method just indicated. Compare the values found in the two cases.

The unaltered cane sugar solution is used to determine the inversion velocity (see p. 106). In order to prevent decomposition a few drops of chloroform, camphor, or thymol are added.

Light absorption.—The Spectro-photometer.

Every coloured substance absorbs light in certain definite regions of the spectrum. The degree of absorption is characterised by the magnitude of the **extinction-coefficient** E, a characteristic constant for every substance and for every part of the spectrum. It is independent of the thickness of layer of the solution δ, and its concentration c.

If the light which falls on a layer of solution has the intensity I_0, that passing out will be

$$I = I_0 e^{-\delta E c},$$

since in every infinitely thin layer an absorption takes place proportional to the thickness and the particular intensity at that layer (a kind of negative compound interest).

It follows that $E = \frac{1}{c\delta} \ln \frac{I_0}{I}$, or if for the sake of convenience the calculation is made with logarithm to the base 10,

$$E' = \frac{1}{c\delta} \log_{10} \frac{I_0}{I};$$

if the specific extinction co-efficient E' has been determined (for $\delta = 1$, and $c = 1$) and the value of $\log \frac{I_0}{I}$ has been measured for another solution of unknown concentration x, and thickness of layer δ, then

$$c = \frac{1}{E'\delta} \log \frac{I_0}{I} \text{ (spectrophotometric analysis).}$$

The absorption of the two solutions can be found by direct comparison with a definite intensity of light from the same source. It is always more convenient, however, to compare two layers of the same solution of different thicknesses. Schulz's trough (Fig. 31) can be used for this purpose, a glass vessel with flat sides parallel to each other, of about 11 mm. internal width. The interior is divided into two unequally thick layers by a 10 mm. thick glass parallelepiped. In using this vessel the loss of light by reflection from the sides need not be taken into consideration. The observed diminution of light will be produced wholly by a layer of liquid of the same thickness as the glass block (δ). If, as is usually the case, $\delta = 1$ cm., and c = one gram per litre, then E is simply

$$= \log_{10} \frac{I_0}{I}.$$

$\frac{I_0}{I}$ is measured by making the two intensities equal; to do this the stronger is diminished by a measured amount. The Schulz's trough is placed in front of the horizontal slit of a spectrum apparatus, with the upper surface of the glass parallelepiped level with the middle of the slit. The light which enters through the lower half of the slit has only passed through 1 mm. of liquid; it is diminished until equal with the other, either by diminishing the width of the lower half of the slit or, preferably, polarimetrically. This is brought about most simply if the light which enters through the whole slit is allowed previously to traverse a polarising calc-spar prism, and a small Nicol, whose rotation can be measured, is placed behind the lower half. If two Nicols are used, and their polarisation directions are inclined at an angle a, *i.e.*, the small Nicol has been rotated through that angle, then it only permits a fraction of the light to pass proportional to $\cos^2 a$ (see p. 84); here, again, secondary loss has not been taken into account. In this case (Hüfner's Photometer) $\frac{I_0}{I} = \cos^2 a$.

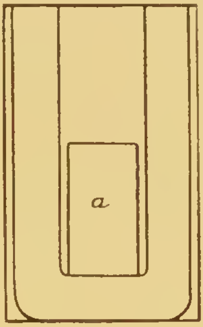

FIG. 31.

Glan's Photometer is a more complex apparatus, but gives more exact results (see Fig. 32).

The light emitted from the lamp (an incandescent burner, covered with a white glass shade, is preferable, or a lens placed at focal distance) passes through the horizontal slit in the collimator tube, in which are fixed in order a lens, an immovable *Wollaston* double prism, and a rotating Nicol, which completely fills the width of the tube. To the Nicol is joined a vernier, which moves over a fixed circular scale. The double prism projects two images from each half of the slit (acting in the same way as natural double spar), and these are polarised vertically to each other; the images lie further apart than would be the case with a natural calc-spar prism. The four slit images, after passing through the Nicol, are split up into the corresponding spectra by the large prism, which has a strong dispersion—and then pass into the telescope. There the two external spectra are screened, so that there only remain two spectra polarised at right angles to each other, and from different halves of the slit. They cut each other at a small angle. By adjusting the collimator and the observation tube, the point of section can be set at any desired part of the spectrum; thus two images from a suitable part of the spectrum for the experiment can be made to cross each other directly by means of the eye-piece adjustment. If the Nicol is rotated round 90°, first one and then the other slit image will be darkened completely, so that a position of the Nicol is obtained for every value of I_0 and I, for which the two slit images have *equal* intensity, in which position no separating line is visible (reading a).

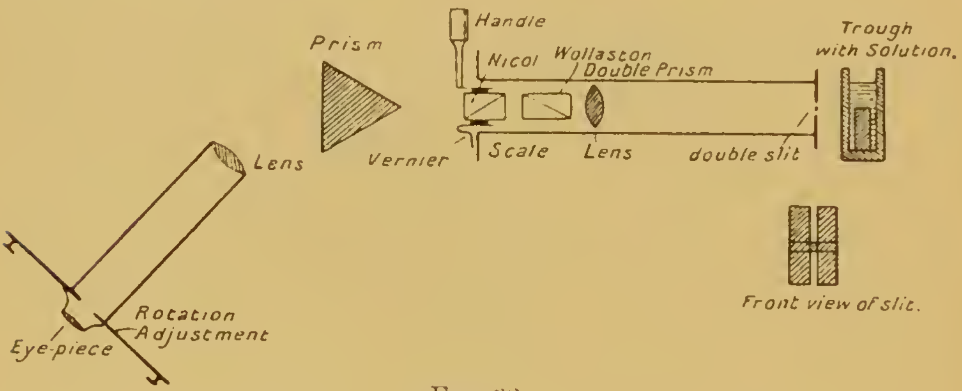

FIG. 32.

The brightness of the one field of vision is $I_0 sin^2\, a$, of the other

$I\ cos^2\ a$, whence $\frac{I_0}{I} = \frac{cos^2\ a}{sin^2\ a} = \frac{1}{tan^2\ a}$. In making exact measurements losses through the different reflections and absorptions must be considered in the calculation. If these are in the ratio of $a : a_0$ for the two rays, then at the position of equal brightness :

$$I_0\ a_0\ sin^2 a = I\ a\ cos^2 a\ ; \ \frac{I_0}{I} = \frac{a}{a_0}\ \frac{1}{tan^2\ a} = k\ \frac{1}{tan^2\ a}.$$

k is determined by lighting both halves of the slit equally strongly, finding the position of maximum darkness for the lower slit (a_1) and the position of equal brightness (a_2). Theoretically $a_2 - a_1 = 45°$ $(k = 1)$. k is equal to $tan^2 (a_2 - a_1)$.

For this purpose a yellow-green light is best, although, strictly speaking, k varies slightly from colour to colour.

Exercise.—An equivalent normal copper sulphate solution is taken, and 10 c.c. transferred to a Schulz's trough. By adjusting the eye-piece the whole of the absorption spectrum is examined, and a suitable portion found within which to determine the molecular extinction coefficient. As zero position the angle is taken at which the lower field of vision appears quite dark (a_1). The solution is diluted step by step by pipetting out 5 c.c. of solution and replacing them with 5 c.c. of water. The student should convince himself of the constancy of the molecular extinction coefficient.

Finally a copper sulphate solution of unknown strength is analysed spectrophotometrically.

Such organic solutions as methyl violet give sharp absorption bands, which can be traced through widely different dilutions.

CHAPTER VI

THE THERMOSTAT

Chemical and physical properties are frequently altered considerably under the influence of temperature. In such cases measurement of these properties must be carried out at a definite temperature. It suffices sometimes to observe exactly the temperature at which a particular measurement is made. Examples are afforded by the series of optical experiments given in the last chapter. More frequently, it is desirable to maintain a definite selected temperature; this is especially the case in the measurement of densities and conductivities, etc., and in the phenomena of catalysis dealt with in the next chapter.

A particular temperature can be maintained in two ways. The first depends on fusion or evaporation of some convenient substance, since such changes always take place at a definite temperature. The chief example of this principle is the production of zero temperature by a mixture of ice and water. The vessel which contains the substance to be cooled to 0° is immersed as much as possible in a bath of finely powdered ice; enough distilled water is added to thoroughly moisten the ice. If the temperature has to be kept constant for a considerable time, some device must be adopted for draining away the water formed, and replacing it with more powdered ice.

In most cases, however, the temperature is maintained automatically; a bath is prepared at the particular temperature desired, and enough heat is added to maintain that temperature if it is above that of the surroundings, or is taken away if the temperature is lower than that of the surroundings. Only the first case is considered here. The liquid used in the *thermostat* is almost invariably water.

A rough thermostat can be constructed easily, which with careful adjustment will give a temperature constant to one-tenth of a degree for several hours. Such an arrangement is sketched in Fig. 33. The bath itself is conveniently a circular tinned iron vessel, such as is frequently used for domestic purposes. It is almost completely filled with water, which is heated best by a luminous gas flame, allowed to play directly on the bottom of the vessel. The gas flame must be carefully screened from draughts. This is done conveniently by surrounding it with bricks, which at the same time serve to support the thermostat. The gas before reaching the burner passes through a part of the regulator. Many regulators have been devised; that shown can be prepared easily by a student with a slight knowledge of glass blowing.

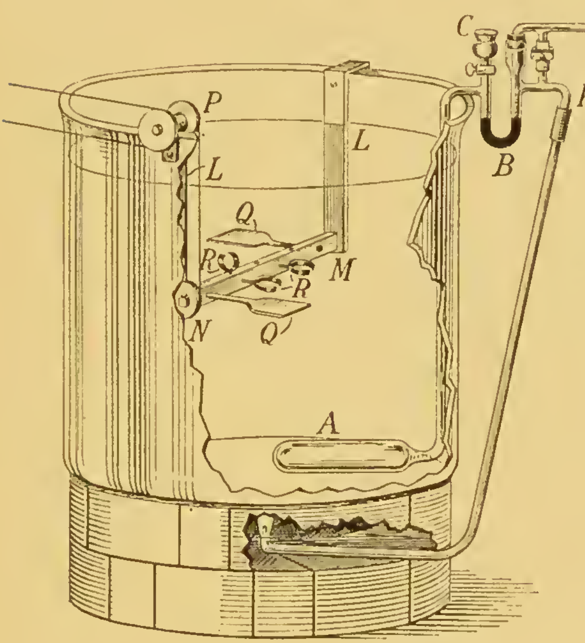

FIG. 33.

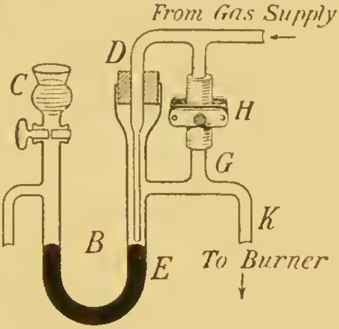

FIG. 33*a*.

It consists of a glass tube *A*, four or five inches in length, and an inch in diameter (the size varies with the size of the thermostat), closed at one end, joined at the other to a thin glass tube which connects it with the glass U-tube *B* (shown enlarged in Fig. 33a.) The bend of the U-tube contains mercury. The side nearest the tube connecting to *A* carries a tap and a funnel *C*, the other side is enlarged slightly, as at *D*, and closed by a tight-fitting cork, through which passes a glass tube, elongated to *E*, and barely touching the surface of the mercury. Its upper end branches into two parts, one connected with a gas supply, the other joined by a piece of rubber tubing to a branch from the **U**-tube, similarly divided at *G*. This rubber tube can be closed, or almost closed, by the screw-clip *H*. The tube *K* is joined by a stout rubber tube to the lead tube leading to the burner. The rubber tube must be wired securely.

A, the connecting tube, the half of the **U**-tube and the reservoir *C*, can be filled with toluene, a liquid which possesses a large coefficient of expansion. More conveniently, *A* is filled completely with chloroform, the connection tube and *C* with water, which of course remains above the surface of the chloroform. All air bubbles must be carefully displaced. To use the apparatus, the thermostat is first filled with water at just above the desired temperature (say 25°). The tap in the **U**-tube is open, and water is added to or removed from the reservoir as necessary, until finally, when the chloroform is in equilibrium with the water in the bath, *C* should be half filled with water; the tap is then closed. Under these conditions the weight of water above the mercury will force it round until it just touches the inserted glass tube at *C*, completely preventing passage of gas through it. The clip *H* is then screwed up to such an extent that the gas jet is only just alight (it must be kept sufficiently large, however, to prevent any risk that the flame be blown out by draughts). If possible this adjustment should be made when the temperature is about a tenth of a degree above 25°. As the temperature falls, the chloroform contracts, with the result that the mercury in the **U**-tube is pulled round until the opening of the inner tube at *E* is exposed. This immediately allows a larger supply of gas to pass, heating takes place, the chloroform expands and pushes the mercury over, and the extra gas supply is again cut off. If the temperature becomes constant slightly below 25°, the inserted tube must be raised somewhat (at *D*); if above 25°, then this tube must be pushed further through the cork. If the flame can be made sufficiently small when the extra gas supply is cut off, and large when it is on, a very constant temperature results. The tap on the **U**-tube can be replaced by a second piece of rubber tubing with clip.

To alter the bath to a new temperature, both tap and clip of the **U**-tube must be opened, the temperature of the bath roughly adjusted by the addition of hot or cold water to a shade above that required, as in the first instance, and the adjustment made as usual. If temperatures above 50° are required, the surface of the water in the bath must be covered with a layer of paraffin, to prevent too rapid evaporation.

Apparatus for Stirring.—To keep the bath constant throughout its bulk not only must the regulating apparatus be adjusted carefully, but the water in the bath must be stirred thoroughly. This can be effected conveniently by some such arrangement as that shown in the figure. It consists of two flat rods of metal *L*, arranged vertically and diametrically opposite, the tops of which are screwed tightly into the top of the thermostat vessel. They support a third metal rod *M*, of square section, placed horizontally, which can rotate freely round its axis. It carries at one end a pulley wheel *N*, which is connected by catgut with a similar wheel *P* fixed above the surface of the water, and moving on the same axle as a third wheel outside the thermostat. This is connected by a band of soft string or catgut with a source of energy. Hot-air engines are very convenient for this purpose, and water turbines can also be used. However, electric lighting is common in physical-chemical laboratories, and by far the most convenient method is through a small motor, driven directly from the main supply.

The horizontal bar carries two or more vanes *Q*, which when caused to rotate by the means described, rapidly agitate the water of the bath, until its temperature is constant throughout. The bar can also be fitted with clips *R*, into which can be fixed closed vessels, containing substances which it is desirable to rotate in the thermostat, in order more quickly to bring about temperature equilibrium, or for some other reason.

Experiment. The Measurement of Solubility.

Regulate the thermostat at 20°. See that it remains constant to a tenth of a degree for at least an hour. Use for this purpose a good thermometer, graduated to tenths, which should be compared previously with a standard thermometer, or its zero point tested by placing it in a mixture of ice and water (cp. p. 94).

The two solubilities most commonly measured are those of gases, or solids, in liquids; a liquid is said to be saturated with respect to a gas or solid when it will dissolve no more of it. In order that saturation may be certain, excess of the substance which is dissolving must always be present, and in order to facilitate this state of equilibrium between solvent and dissolved substance, the two phases must be brought into contact with each other as much as possible, by vigorous shaking, and by employing solids in the state of fine powder. Only the case of solids is here dealt with. To obtain accurate results it is essential that the measurements are carried out in a thermostat, since the solubility of most substances varies largely with temperature.

While the thermostat is being tested, in order to see that the temperature adjustment is correct, take two stout test tubes (short, flat-bottomed specimen tubes are recommended), and fit them with tight-fitting indiarubber corks.

Powder finely in different mortars sodium chloride and oxalic acid. Rinse out the two tubes carefully with distilled water, and transfer several grams of each solid to one of the tubes. Then fill them about two-thirds full of distilled water (the tubes must be etched or distinguished in some way), tightly cork them, and, if the thermostat is in good order, fix them in the clips in the horizontal bar. Observe them from time to time to see that excess of solid remains (if all the solid dissolves, the tubes must be removed, dried, opened and more solid added, and replaced in the thermostat. They should rotate for at least an hour without further addition of solid, and in presence of excess. Then remove them from the clips and fix them in a wire cage or some similar arrangement with the corks just above the surface of the water. There they should be allowed to remain ten minutes or a quarter of an hour, until the excess solid has in great part sunk to the bottom.

Meanwhile dry and weigh a stoppered flask, also a small porcelain crucible contained in a stoppered flat-bottomed weighing vessel. Take two 2 c.c. pipettes, dry them and cover their nozzles with filter paper. Next open the tube containing oxalic acid, insert a pipette just below the surface of the liquid, pipette out 1—2 c.c. of liquid, remove the filter cap (which has kept back any floating solid) and transfer the liquid to the stoppered flask, which must be immediately closed. In the same way transfer a similar quantity of sodium chloride solution to the crucible; the containing weighing vessel must also be closed at once. Weigh both vessels. The amounts of solution are thus found.

Take out the crucible containing sodium chloride and evaporate it to dryness over a water bath. Finally heat it to a slightly higher temperature, and allow it to cool inside the weighing vessel. Again weigh; the amount of solute is thus found. If the solute weigh x grams, and the solution y grams, then the number of grams of solute to 100 grams of solvent will be $\frac{100\,x}{y-x}$. In order to find the number of gram molecules of solute per 100 gram molecules of solvent it is necessary to divide by the respective molecular weights. If these are X for the solute, Z for the solvent, then this quantity will be

$$\frac{100\,x\,Z}{(y-x)\,X}.$$

Titrate the oxalic acid solution with standard baryta solution, using phenolphthalein as indicator. Calculate the amount of oxalic acid in 100 grams of solution, and then determine the number of grams per 100 gram solvent, and the number of gram molecules per 100 gram molecules of solvent.

Repeat each solubility determination. The agreement should be well within 1 per cent. Adjust the thermostat to 25°, and finally to 30°, making solubility determinations at each temperature.

The solubility of sodium chloride does not increase much with rising temperature, since the heat of solution is very small (see p. 57). The heat of solution of oxalic acid is greater, and its increase of solubility with rising temperature is marked.

If pure alcohol is used as solvent, or any other liquid which appreciably dissolves india-rubber, the glass tubes must be replaced by small, stout glass bottles, with ground glass stoppers, which are tightly fixed by means of stout rubber bands.

CHAPTER VII

CHEMICAL STATICS AND DYNAMICS

CHEMICAL statics and kinetics, the theory of equilibrium and the way in which equilibrium becomes established, are based on the **law of mass action.** If four substances react according to the scheme $A + B \rightleftarrows C + D$, *i.e.*, if the reaction is reversible, then, according to the law, when a state of equilibrium is attained,

$$\frac{\text{Concentration of } A \times \text{concentration of } B}{\text{Concentration of } C \times \text{concentration of } D} =$$

$$\frac{[A]\,[B]}{[C]\,[D]} = \text{constant.}$$

The velocity V by which this equilibrium is attained, the velocity of reaction, is equal to the difference of the velocities of the two oppositely directed reactions v and $v.'$ This of course is

$$V = v - v' = k\,[A]\,[B] - k'\,[C]\,[D].$$

For equilibrium $V = o$, and the formula becomes that already given.

Where a binary electrolyte dissociates, the equation of the reaction is:

$$\text{Molecule} = \text{Cation} + \text{Anion}.$$

Since, however, the concentration of both ions is equal, it is possible to write

$$\frac{(\text{Concentration of ions})^2}{\text{Concentration of undissociated part}} = \text{const.}$$

$$= \text{the constant of dissociation};$$

(for the measurement of this see p. 137).

The concentration of a dissolved substance is reckoned in number of molecules of the substance per litre of solution; for a gas, its partial pressure is taken. If only a single molecule reacts, and the reaction proceeds practically in *one* direction alone (transformation, or decomposition), the velocity of the *monomolecular* reaction is

$$v = k\ [A],$$

and is therefore proportional at any time to the amount not transformed, or undecomposed at that time.

If the amount at initial time ($t = o$) is a, and at time t is $a - x$, then $$\frac{dx}{dt} = k\ (a - x).$$

By integration $$k = \frac{1}{t} \ln \frac{a}{a - x}.$$

If two molecules react (a *bimolecular* reaction), and if the substances are initially in molecular proportions, then

$$\frac{dx}{dt} = k\ (a - x)^2, \text{ and } k = \frac{1}{t} \frac{x}{(a - x)\ a}.$$

If the original concentrations are different, and in the ratio $a : b$,

$$\frac{dx}{dt} = k\ (a - x)\ (b - x) \text{ and } k = \frac{1}{(a - b)\ t} \ln \frac{(a - x)\ b}{(b - x)\ a}.$$

Reactions higher than the second order occur but seldom.

Qualitative Proof of the Law of Mass Action.

(a) *in Gases.*

In an evacuated and sealed glass bulb of about 250 c.c. capacity are placed 10 grams of phosphorus pentabromide; in a second similar bulb 8 grams of the pentabromide, and 2 of the tribromide. On evaporation the pentabromide dissociates according to the equation—

$$PBr_5 = PBr_3 + Br_2,$$

so that $$\frac{[PBr_3]\ [Br_2]}{[PBr_5]} = \text{const.}$$

If the concentration of the tribromide is increased, as in the second bulb, the concentration of the bromine must decrease, that of the pentabromide increase, *i.e.*, *dissociation is lessened.*

Both bulbs are placed in water at about 90°; it is apparent that the pentabromide in the first vessel is largely dissociated, since it shows distinctly the colour of bromine vapour (comparable with a flask half filled with bromine water), while the colour of the bromine vapour in the second flask is much lighter (straw yellow).

(b) *in Solution.*

Dry ligroin is shaken up with dry picric acid. The solution which results is nearly colourless (*the colour of the undissociated acid*). Water is added, and the solution again shaken up; the accompanying dissociation of the acid shows strongly the yellow *colour of the anion.* If strong hydrochloric acid is added, the solution again becomes colourless (decrease of dissociation, etc.). Addition of alkali to a second aqueous solution increases the yellow colour, since the alkali picrate is more strongly dissociated than the picric acid.

Every acidimetric and alkalimetric titration has as basis the law of mass action (influence on dissociation); each case of hydrolysis, etc., is based on the same law. For similar cases see analytical handbooks.

Statics.

Decrease of Solubility due to the Addition of a Common Ion.

If a salt is added to a saturated solution of a difficultly soluble binary electrolyte, which has an ion in common with it, it follows from the law of mass action that the dissociated portions of both salts must partly recombine. Since the undissociated part of the difficultly soluble salt has a limited solubility, which is already attained in a saturated solution, an amount of salt will be precipitated corresponding to the decrease in dissociation, *i.e.*, the solubility becomes less. This principle has repeated applications in quantitative analysis. If a small quantity of salt is added which has no ion in common, it has no influence on the solubility of the first; neither, practically, has a substance which can yield one of the same ions, but is dissociated only to a very slight extent. The general formula can be found in handbooks of physical chemistry. Here only a specially simple case will be discussed and an approximate experimental proof undertaken.

Consider two salts, possessing a common ion, equally strongly and nearly completely dissociated, and of such dilution that the law of mass action is strictly applicable. In order to obtain distinct conditions, the solutions are mixed in such proportions that equal amounts (n) of the differing ions are present, while in the pure solution of the difficultly soluble salt there were n_0 ions. Then according to the law of mass action, since the concentration of the undissociated part remains unaltered, the constant ion product is

$$n_0^2 = n\,(n + n).$$

The mixed solution really contains n ions of the same sign, but $2n$ ions with opposite sign. Hence

$$\frac{n_0}{n} = \sqrt{2} = \text{about } 1{\cdot}41 \text{ and } \frac{n}{n_0} = 0{\cdot}71.$$

If a quantity of the second salt corresponding to 0·7 of the saturation-concentration of the first is added to a saturated solution of the first, equal quantities of the two salts will be dissolved at their saturation point.

If dissociation is incomplete, the conditions become more complicated, since a constant amount of the less soluble salt remains undissociated, but the dissociation of the second salt is less than the normal value. When the concentration of the two differing ions is the same in the mixed solution, it is twice as great as in the pure solutions of equal ion content.

If the two salts are not dissociated to the same extent, the conditions are less distinct. However, it is perhaps possible, without great error, to assume equal dissociation in salt solutions of equal dilution.

Again, if first a quantity of salt with like cation is added to a saturated solution of a slightly soluble salt, and then the corresponding amount of a salt with like anion, both additions must lessen the solubility to the same extent.

A convenient quantitative proof of the theory is obtained with **silver acetate**; the saturated solution at 20° is 1/16 n. and, according to Arrhenius, is 90 per cent. dissociated. To prepare a saturated solution the solid and water are shaken together for two hours to produce equilibrium. The solution can be titrated easily by Volhard's method. Three convenient types of compound for addition are silver nitrate, sodium acetate, and acetic acid; potassium nitrate can be used as a fourth indifferent substance with no ion in common.

Excess of salt is placed in each of five flasks (previously thoroughly steamed out and dried, see p. 12), fitted with glass stoppers, and of about 150 c.c. capacity. To the first flask is added 100 c.c. water, to the second the same quantity of 0·046 n. silver nitrate solution, to the third a sodium acetate solution, to the fourth an acetic acid solution, both of the same concentration as the silver nitrate, and to the fifth a potassium nitrate solution. The solids can be weighed out, and added in each case with 100 c.c. of water. Each flask is warmed in a water bath at about 50°, and shaken occasionally, finally removed, cooled slightly, and closed with a tightly-fitting rubber stopper. It is then rotated for two hours in a thermostat at 20° in the manner already described (see p. 102). The solid in the flasks is allowed to settle as usual, and an adequate amount of solution pipetted out for titration. (In this case the volume measurement is sufficiently correct.)

The titration shows that in point of fact the silver nitrate and sodium acetate do produce the same decrease in solubility, whilst the two other substances are almost without effect. Acetic acid is only dissociated to the extent of 2 per cent. at the concentration of the experiment, and its influence on the solubility is therefore well within the limit of error.

The concentration of $Ag^{\cdot}$- and CH_3COO'-ions in the pure solution is about 0·062 × 0·9 = 0·056, and that of the undissociated portion in consequence about 0·006. The ionic concentration in the mixed solutions, in so far as the ions are produced from silver acetate, is found when 0·006 is subtracted from the total concentration (after the deduction of the silver nitrate added). It is diminished to about 0·7 of the original value. In a 0·046 n. solution of silver nitrate or sodium acetate, the concentration of the undissociated part is about 0·003, and hence in the mixed solution 0·006, like that of the undissociated silver acetate. The additions in point of fact give a value for the ionic concentration not far from 0·04 = 0·056 × 0·71, so that it actually happens that $\frac{n_0}{n} = \sqrt{2}$. An accurate result is not to be expected, since the solutions employed are not sufficiently dilute for strict adherence to the law of mass action. And further, the additions are dissociated a little more strongly than the silver acetate.

A closer example is found in the influence of solubility in very dilute solutions (see later, p. 140, and also p. 161).

The Transition Temperature.

According to the *phase rule*, the degrees of freedom of a system plus the number of phases, are equal to the number of components plus two ($P + F = C + 2$).

It follows that in a system built up from a single component, if there are three phases the degree of freedom is zero, *i.e.*, the three phases can co-exist once, and once only, under the accompanying conditions of temperature and pressure. The same is true for two components and four phases.

Hence, if the maximum number of phases are brought together (solids must be powdered and thoroughly mixed) the equilibrium temperature must be produced, and if the mixing is maintained it will remain constant until one phase in some way disappears.

Such a constant temperature is used in thermometry, *e.g.*, 0°, the zero-point of our definition of temperature, is a case of such an equilibrium (one component in three states of aggregation, *i.e.*, three phases).

Exercise.—Determine the two equilibrium temperatures in the system $Na_2SO_4 - H_2O$, thermometrically. The four phases at the first quadruple point are—ice, Glauber's salt, saturated solution, water vapour (the cryohydrate point) ; at the second—Glauber's salt, the anhydrous salt, saturated solution, and water vapour (transition point).

The student should convince himself that the temperature of equilibrium is independent of the *amounts* of the components, so long as these amounts are so large that all four phases co-exist.

Remarks.—Where a direct determination of the transition temperature is not possible, on account of the slowness of reaction, the temperature is found at which the saturated solutions of both modifications become identical. Any conveniently applied property of the solution can be employed for this purpose: concentration, density, refractive index, vapour pressure (with a tensimeter), conductivity, etc., or, again, the perceptible change of volume is used as a criterion. This is observed in a *dilatometer*, an instrument of the nature of a thermometer, consisting of a reservoir (a glass tube of $\frac{1}{2}$—$\frac{3}{4}$ inch diameter and five or six inches in length), joined to a capillary. To the latter a scale is pasted. The reservoir is nearly filled with a mixture of the two modifications, moistened by a little of the solution, and the whole is filled, by means of an exhaust pump, with an indicator liquid such as petroleum or a paraffin. The dilatometer is then placed in a constant temperature bath. Two temperatures are sought, at which the meniscus in the capillary changes in opposite directions, *i.e.*, at which the transition point is approached from different directions. These two temperatures are then made to approximate more and more closely to one another, until finally the true transition point can be interpolated.

However, in by far the most cases, identity methods (especially the most accurate, the tensimetric), as well as dilatometer methods, are too lengthy and inconvenient for a practical course.

Kinetics.

Inversion Velocity of Cane Sugar.

Under the catalytic influence of hydrogen ions, cane sugar hydrolyses according to the equation:

$$\text{Cane sugar} + \text{water} \longrightarrow \text{glucose} + \text{fructose}.$$

The reaction is in consequence bimolecular. If, however, a dilute solution is used (with the large molecular weight of cane sugar, a 10 per cent. solution is relatively dilute) the change in concentration of water is inappreciable, and the reaction becomes apparently monomolecular. The increase of invert sugar takes place according to the equation

$$\frac{dx}{dt} = k\,(a - x)\ ;\ k = \frac{1}{t}\ \ln \frac{a}{a - x}\ \text{(see p. 101)}\ ;$$

since k varies with the amount of the catalytic agent, *i.e.*, of H-ions, measurements of k can be used to compare the strengths of two acids.

Here the measurement of k for only *one* acid solution will be considered.

20 c.c. of the solution of cane sugar already employed (see p. 89 *et seq.*) is mixed with 20 c.c. of about $2n$ hydrochloric acid solution, and the actual time of mixture noted. At this time, $t = 0$, the corresponding amount of invert sugar $x = 0$. The amount of cane sugar is known from the rotation, which is half the value found in the former solution. The mixture is placed in a polarisation tube, with a cooling jacket, and the polarisation measured at 20°. Initially the rotation decreases rapidly. The uncertainty lies in the measurement of the angle, not in that of time. In order to obtain corresponding values relatively accurate, the following plan is adopted:—

The analyser is placed in position, the time noted, the angle read and noted, the time again noted, and a second reading taken and noted. The adjustment, angle measurement, and time observations are made at about equal periods, so that the mean of the two angle measurements accurately corresponds to the mean of the two time observations.

After about five minutes a further reading is made, afterwards others at longer intervals. The observed values for a and t are plotted on squared paper; with careful work a regular curve is obtained. The tangent to the angle of incidence at any time is proportional to the amount of cane sugar present.

What portion of the curve is most advantageous and least subject to error for the calculation of the inversion constant k?

k should be determined from each observation according to the following method:—Let the initial rotation at the moment of mixing be a_0 (found as at p. 89) and the (unobserved) final rotation $-E$ (calculated as shown there). Let a be the angle measured at time t. The original amount of cane sugar is proportional to $a_0 + E$, the corresponding amount at time t, to $a + E$. Hence

$$k = \frac{1}{t} \ln \frac{a_0 + E}{a + E}; \text{ or } = \frac{\log_{10}(a_0 + E) - \log_{10}(a + E)}{0{\cdot}4343\, t.}$$

If the time of mixing t_0 has not been observed accurately, a pair of trustworthy observations, t_1 and a, can be taken as initial values. In this case

$$k = \frac{\log_{10}(a_1 + E) - \log_{10}(a + E)}{0{\cdot}4343\,(t - t_1)}.$$

Hydrolysis of Methylacetate by Sodium Hydroxide.

A sodium hydroxide solution about $\frac{1}{40}\,n$ is prepared from metallic sodium, and in this way is obtained free from carbon dioxide;* a $\frac{1}{50}\,n$ solution of ethyl acetate is also prepared. 250 c.c. of each solution are transferred to well-dried wide-necked flasks, which are placed in a bath at 20° until that temperature is attained. Meanwhile the apparatus for titration is prepared. $\frac{1}{25}\,n$ HCl, and $\frac{1}{50}\,n$ NaOH are employed, and are carefully standardised against one another. From the hydrochloric acid solution several quantities of 20 c.c. are pipetted into glass beakers and are cooled. When both the solutions have attained the temperature of the thermostat, they are mixed, thoroughly shaken, and 50 c.c. pipetted out immediately ; for the sake of rapidity, the solution is allowed to flow from the inverted pipette into one of the glass beakers containing the acid. The initial time is reckoned from this point. The excess of acid is titrated against the $\frac{1}{50}$ n NaOH, using phenolphthalein as indicator. After some minutes a second 50 c.c. is removed, and treated in the same way. The time interval between each measurement is chosen somewhat longer. The number of c.c. NaOH employed in the back titration must be perceptibly different. After the seventh 50 c.c. has been removed and tested, the remaining solution is placed in a well-corked flask and warmed for about an hour in a water bath ; by this time all the ester becomes hydrolysed, and the excess of NaOH can be measured. After the solution has cooled, two titrations are made, each with 50 c.c. In this case it is unnecessary to pipette into excess of cold hydrochloric acid ; the purpose of this operation was merely to stop the reaction. It is desirable to do so, however, in order to carry out the whole series of determinations in a similar manner ; in this way all the titrations are made with dilute solutions, and the end point is approached from the same side.

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* A clean dry platinum dish is placed in a desiccator containing dilute aqueous sodium hydroxide. The desiccator is closed with a soda-lime tube. The calculated quantity of sodium is placed in the dish in the form of thin slices, carefully freed from adhering petroleum by blotting paper. The metal appears to have melted after about half a day. The concentrated solution thus formed is transferred to a measuring flask and diluted to the requisite extent with freshly boiled distilled water.

Let the number of c.c. HCl (after taking into consideration the number of c.c. of NaOH used in the back titration) be

in the first titration ($t = o$) c_o,

in the later titrations (time t) c,

in the last titration (corresponding to time ∞), as average value c_e,

then the quantity of soda solution at the beginning of the reaction will be c_o c.c, the initial quantity of ester $(c_o - c_e)$, and at the different times t, the respective quantities changed will be $(c_o - c)$ c.c.

In the formula for a bimolecular reaction (p. 101), the following values must be substituted :—

for a, c_o ; for b, $(c_o - c_e)$; for x, $(c_o - c)$.

The result is obtained

$$k = \frac{1}{c_e t} \ln \frac{c\,(c_o - c_e)}{(c - c_e)\,c} ; \text{ or}$$

$$k = \frac{1}{0{\cdot}4343\ c_e t}\Big[\log_{10} c + \log_{10}(c_o - c_e) - (\log_{10} c_o + \log_{10}(c - c_e))\Big]$$

If ester and soda are present in nearly equal quantities, the simpler formula can be used,

$$k = \frac{1}{t}\,\frac{x}{(a - x)\,a}, \text{ which becomes}$$

$$k = \frac{1}{t} \cdot \frac{c_o - c}{c \cdot c_o}.$$

If the quantities are not exactly equivalent, the concentration is taken equal to the amount of substance present in the less concentrated solution. In this case, however, the constant changes perceptibly, especially towards the end of the reaction.

ELECTRO-CHEMISTRY

CHAPTER VIII

FOUNDATIONS

THE **standard electromagnetic units,** *i.e.*, the units which relate to moving electricity, are

the *Ampere* (A), unit of current intensity i;
the *Ohm* (Ω), unit of resistance r;
the Volt (V), unit of potential, or of electromotive force e.

They are related to one another by *Ohm's Law*, according to which $\frac{e}{r} = i$; *i.e.*, an electromotive force of one volt produces in a circuit of which the resistance is one ohm a current intensity of one ampere.

These units have been obtained from those originally defined by Weber in the C.G.S. system; in order to make them more practicable, and the numbers less unwieldy, they were multiplied by powers of ten. The C.G.S. unit of current intensity was multiplied by 10^{-1}, that of electromotive force by 10^{8}, and in consequence that of resistance by 10^{9}, since Ohm's Law should also hold for the new units.

The resistance of one ohm is defined legally as the resistance of a mercury column of one square millimetre cross section, and 1·063 metre length, at 0° (weight of mercury in vacuo 14·4521 grams). The old *Siemens'* unit or mercury unit was the resistance of a mercury column one metre long and one square millimetre cross section at 0°. This is no longer in use, but is still found in old publications and laboratory apparatus; to obtain true *ohms* numbers depending on the old unit must be divided by 1·063.

At one time, when the comparison between Siemens' unit and Ω was not completed, some physicists used the "legal ohm"; the corresponding column of mercury was 1·060 metres long.*

The *Ampere* is defined as the intensity of a constant current which deposits 1·118 mg. silver per second in a silver voltameter (see p. 143).

The *Volt* is then defined by Ohm's Law. It is the electromotive force (E.M.F.) which produces a current of one ampere intensity in a circuit of one ohm resistance. A normal element (see p. 152) of the composition: mercury, mercurous sulphate, cadmium sulphate, a saturated cadmium sulphate solution, cadmium sulphate, and a 10 per cent. cadmium amalgam, has at 15—20° an average E.M.F. of 1·0187 volts (more exactly $e = 1{\cdot}0187 - 0{\cdot}000035\,(t - 18) - 0{\cdot}00000065\,(t - 18)^2$ volts). If the cadmium is replaced throughout by zinc, then the E.M.F. of the element at 15° is 1·4328, at 18° 1·4292, at 20° 1·4265 volts ($e = 1{\cdot}4292 - 0{\cdot}00123\,(t - 18) - 0{\cdot}000007\,(t - 18)^2$ volts).

If **Ohm's Law** is used in the form $e = ir$, for a closed circuit, of which the resistance is composed of two parts (r_1 and r_2) joined together, it follows, since the current intensity is the same throughout the circuit, that

$$e_1 = ir_1\,;\ e_2 = ir_2\,;\ \text{whence}\ \frac{e_1}{e_2} = \frac{r_1}{r_2}\,;\ r_1 + r_2 = r\,;$$

$$e_1 + e_2 = e.$$

That is to say, the fall of potential along any part of a circuit is proportional to the resistance of that part. Consequently, if the internal resistance of an element is r_i and its poles are joined externally by a resistance r_a, then $i = \dfrac{e}{r_i + r_a}$, and the fall of potential in the outer circuit

$$e_a = ir_a = \frac{er_a}{r_i + r_a}.$$

Unless, therefore, the external resistance is not infinitely great compared with the internal, a part of e will be used up inside the element, in order to overcome the internal resistance, *i.e.*, the "available potential" is smaller than the E.M.F.

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* In practice not mercury columns but wire resistances are always used.

The numbers given for the normal elements are valid only for the case in which the external resistance is infinitely great.

Quantity of Electricity is the product of current intensity and time. Its unit is the ampere-second or the *Coulomb*. Since a coulomb corresponds to 1·118 mg. silver, to a gram-molecule of silver, 107·93 grams, correspond 96540 coulombs.

From *Faraday's Law* (see p. 142) equal quantities of electricity set free equivalent amounts of elements, hence to each gram equivalent set free by a current correspond 96540 coulombs (charge of each equivalent ion).

If a current of one ampere flows through a wire, between the ends of which there is a difference of potential of one volt, the current per second produces an effect of one volt-ampere, or $10^8 \times 10^{-1}$ C.G.S. units, *i.e.*, of 10^7 ergs = 1 watt per second. If the effect is measured calorimetrically, it is equal to 0·2387 g. cal. per second, since the water-gram-calorie at 15° corresponds to $4·190 \times 10^7$ ergs. A watt-second or a volt-coulomb is consequently equal to 10^7 ergs or 0·2387 g. cal.

In order to separate a gram equivalent of an ion, 96540 coulombs must be taken from an element of 1 volt potential, whereby 96540 volt-coulombs of work are performed, which equal, expressed in heat units, $96540 \times 0·2387 = 23050$ gram calories. The gas constant R, which holds for dissolved substances if osmotic pressures are used, consequently, in electrical units (**the electrolytic gas constant**), becomes equal to $\frac{1·985}{23050} = 0·861 \times 10^{-4}$ [watt-seconds T^{-1}]. In this case the unit is not the gram-molecule but the gram-equivalent.

The unit of electrical conductivity (commonly shortened to **conductivity**) (κ) is $\frac{1}{1\ \Omega}$, the reciprocal ohm (sometimes written Mho).

If the resistance of a solution between two electrodes of one square centimetre cross-section, at a distance of 1 centimetre, is one Ω, the solution will possess unit conductivity. At ordinary temperatures, however, the solutions of greatest conductivity do not conduct quite so well as this. *E.g.*, a saturated solution of common salt has at 15° the conductivity 0·20, at 25° 0·25. Since the resistance r is proportional to the length l, and the cross-section q, and inversely proportional to the specific conductivity κ the relation exists :—

$$r = \frac{l}{q\kappa} \text{ and } \kappa = \frac{l}{qr}; \ \kappa r = \frac{l}{q}.$$

In order to make the conductivity independent of the concentration, it is customary to calculate from unit concentration. This is defined electrochemically as the concentration of a solution such that 1 c.c. contains 1 gram equivalent of dissolved substance (a case which can never be realised). Thus, consequently, for the sake of the C.G.S. system (and in order to use more convenient numbers), the unit is not the litre, but the cubic centimetre. A solution which is, in ordinary chemical terminology equivalent normal, will consequently have the concentration $\frac{1}{1000}$.

The conductivity reckoned from unit concentration is termed the *equivalent conductivity*, and this for binary electrolytes, which are those chiefly employed, is in consequence equal to the **molecular conductivity.** It is denoted by Λ. Λ increases with dilution at first rapidly, then more and more slowly, and reaches finally a limiting value, the *molecular* (or *equivalent*) *conductivity at infinitely great dilution*, Λ_∞. If it be assumed that the mobility of each carrier of current, which according to Kohlrausch is independent of the presence of other current carriers, also does not vary with the concentration, then $\frac{\Lambda}{\Lambda_\infty} = a$, the **degree of dissociation,** a relation which makes the conductivity one of the most useful magnitudes in physical chemistry.

Experimental.

The following simple experiment can be used to show that the molecular conductivity, and with it the degree of dissociation, increases with dilution. Two strips of zinc are suspended inside an accumulator vessel so that they touch the bottom. The tops of the strips are bent over the edge, so that they occupy fixed positions. A concentrated solution of zinc sulphate is pipetted into the bottom of the vessel. One pole of an accumulator is laid on one of the zinc strips, and on the other a rough galvanometer, and the circuit is completed—a resistance may perhaps be inserted—by connecting the other pole of the accumulator with the second binding screw of the galvanometer. The deflection of the galvanometer is proportional to the conductivity of the zinc sulphate solution. If water is added, of course the solution is made more dilute, and at the same time the effective cross-section of the cell is increased, so that if the molecular conductivity of the solution, and with it the degree of dissociation, remain constant, then also the galvanometer deflection, which is proportional to the strength of the current, will not be altered. Actually the galvanometer is repelled the more strongly the larger the amount of water added.

In the system zinc—zinc sulphate—zinc no gas is disengaged at the electrodes, since the system remains totally unaltered, and only changes of concentration take place, which, however, compensate themselves. The same kind of experiment can also be used to show that the different conductivities of some typical solutions increase by different amounts with dilution and neutralisation.

A concentrated solution of ammonia gives a slight deflection, which becomes relatively strong on dilution. The same is true for acetic acid. With equivalent solutions of HCl, NaOH, and NaCl, employed as described above, deflections are obtained over a considerable range of magnitude; that for HCl is greatest, that for NaCl least; on dilution each is scarcely altered. The deflection for monochloracetic acid is less, but the increase on dilution is relatively greater. If the (weakly conducting) solution of ammonia is neutralised with HCl or acetic acid, the final deflection, and consequently the molecular conductivity of the salt solution formed, is almost the same; it is much greater than the conductivity of the base, greater than that of ammonia plus acetic acid, less than that of ammonia plus hydrochloric acid.

If an equivalent quantity of soda solution is employed, the end deflections are somewhat similar to those with ammonia, but the conductivities of the salts are always smaller than that of the base (see Tables, Mobilities of Ions, and Molecular Conductivities, pp. 189, 190).

As proposed by Faraday, the plates of metal which are immersed in a solution, and from which the electricity passes into the solution, are termed **electrodes**.

We distinguish between *anode* and *cathode*, or positive and negative poles (see below). The chemical particles which move with the current, and which alone act as carriers of current in solutions, are called **ions**. Metals and hydrogen migrate with the current, migrate down; these are called *cations*. The acid radicals *or* hydroxyl group, *anions*, migrate up.

In a solution of $CuSO_4$ the cation is the bivalent Cu ion, laden per gram-atom with 2 × 96540 coulombs, not, as Berzelius supposed, CuO; the anion is SO_4, not SO_3 (Cu^{++} or $Cu^{\cdot\cdot}$; $^{-}SO_4^{-}$ or SO_4'').

The cations, metals and hydrogen, discharge themselves and are set free at the cathode, the anions at the anode, the positive pole. In accordance with this chemical definition, it is possible to test which pole is the anode, and which the cathode, by chemical means. For the test the so-called *pole reagent paper* can be used, either moist filter paper, on which has been placed a small crystal of potassium iodide, or paper soaked in a solution of sodium sulphate and phenolphthalein. Bright clean ends of wires joined to the poles are laid on the paper, and it is observed at which of them colour is developed. With potassium iodide paper colour develops round the wire connected with the anode (due to the formation of iodine), with Na_2SO_4 paper at the cathode wire, since the Na first produced reacts with water to give NaOH and H, and thus the phenolphthalein becomes coloured red.

Theory of Electrolytic Dissociation.

It was known for a long time that solutions which conduct current without decomposition contain free ions, which are not necessarily split off from the molecule by the current. Arrhenius boldly and ingeniously combined electrochemical phenomena and van 't Hoff's osmotic theory of solution, and showed that in every conducting solution the dissolved molecules are partly dissociated into ions, and that for any particular solution the degree of dissociation depends only on the concentration and the temperature. He also was the first to show how the degree of dissociation could be calculated quantitatively from osmotic or (more conveniently) electrical data, and he showed, further, that all chemical and physical properties of solutions are at once explained by this theory.

Van 't Hoff, Ostwald, and Planck showed simultaneously and independently that in each solution there is a certain equilibrium between ions and undissociated molecules, regulated by the law of mass action, and measured conveniently by conductivity methods.

By subsequent development of the osmotic and dissociation theories, Nernst was able to explain all the potential differences between solutions and electrolytes. In this way it has become possible to calculate the electromotive forces of concentration cells (see p. 158) and to find a great many data useful for inorganic and analytical chemistry.

The dissociation theory at first was received very sceptically everywhere, but has gradually become accepted, and has disclosed new relationships through the whole of chemistry, physics, and physiology, suggesting new explanations and ideas (cp. also the exercises on thermochemistry, pp. 57—62).

Branching of Current. Applications.

1. If a current branches at any point, the sum of the intensities of the currents flowing to that point is equal to the sum of the intensities of those flowing from it.

2. If the electrical currents and forces which flow in one direction in a closed portion of a branched circuit are called positive, those which flow in the opposite direction negative, then the sum of the products of the single resistances into the

corresponding current strengths is equal to the sum of the E.M.F.'s.*

In the accompanying diagram *E* represents an element of E.M.F. *E*, *G* a measuring instrument (a galvanometer); the spiral lines represent the three resistances *R*, R_1 and R_2 of the three parts of the circuit net. If the difference of potential between *A* and *B* is *e*, then,

$$i_1R_1 = e, \text{ and } i_2R_2 = e, \text{ whence } \frac{i_1}{i_2} = \frac{R_2}{R_1}.$$

Further,

$$I = i_1 + i_2 = e\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = i_1\left(1 + \frac{R_1}{R_2}\right).$$

If R_2 is made small compared with R_1, then i_1 will be small compared with *I*. Consequently, if the galvanometer is a delicate instrument, it is possible to measure much larger currents than by direct insertion, if it is arranged in parallel with a suitable resistance. If, for example, R_2 is taken exactly $\frac{1}{99}$ of the galvanometer resistance R_1, then $i_1 \cdot 100 = I$, *i.e.*, a current 100 times as great can be measured as would be possible if the galvanometer was placed directly in the circuit. Its range of measurement has thus been increased one hundredfold. The arrangement is termed **galvanometer with shunt.** If an instrument for measuring potential, a *voltmeter* (*e.g.*, an accumulator tester), of resistance R_1, is connected to the ends of a resistance R_2 (*e.g.*, a 1 Ω resistance), then by Ohm's Law the instrument records a fall of potential proportional to R_2 ($e = ir$); since, however, $R_2 = 1$, the voltmeter with this arrangement gives the current strength in amperes. Strictly speaking, a correction should be applied for the current passing through the voltmeter, which is thus removed from the main circuit (*EBA* and R_2); this amounts to

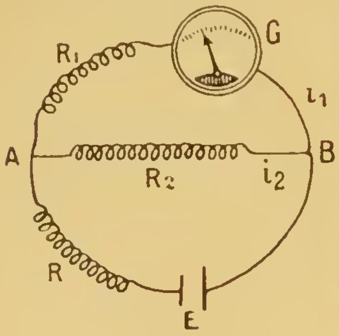

FIG. 34.

$$I = i_2\left(1 + \frac{R_2}{R_1}\right).$$

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* These two laws are due to Kirchhoff.

If the resistance of the voltmeter is 200 Ω, and it is connected to a strip of circuit of 1 Ω resistance, $\frac{1}{200}$ of the observed current must be added.

If it is desired to increase the range of measurement of a potentiometer, or voltmeter, a shunt is *not* employed, but a convenient resistance is placed in *series* with the instrument. If r is the resistance of the measuring instrument, the range will be doubled (the sensitiveness halved) if a resistance of r Ω is joined. One-half of the potential fall will take place in the resistance added, the other half in the instrument itself. By the addition of $9r$ the range will be increased ten times.

In order to obtain from a large potential a smaller amount, the potential is applied to a resistance, *e.g.*, a stretched wire of considerable resistance, and the potential fall from a part of the wire used. Suppose, for example, a lead accumulator (2·0 volts potential) is available, but only 1·64 volts are required. The accumulator is connected with a 1 metre long stretched wire, and two sliding contacts with screw connections are arranged on the wire 82 cms. apart; then the desired potential fall takes place between the two binding screws, which can be made equal to any particular value by simply sliding the contacts. With a plug resistance box (rheostat) the adjustment is less convenient, and not so continuous.

If two resistances r_1 and r_2 are placed in series, the effect is simply added (similarly with two electromotive forces, see below). If the resistances are arranged in parallel, the current intensity in the main circuit, of which the resistance is negligible compared with r_1 and r_2, is:—

$$I = e\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \text{ or } e\,\frac{r_1 + r_2}{r_1 r_2}.$$

It is apparent that if r_1 is small compared with r_2 a relatively large alteration of r_2, and consequently a relatively large shift of the contact, amounts to little.

Hence by regulating r_1, a coarse adjustment is obtained, by decreasing or increasing r_2 a fine adjustment.

If n elements are arranged in series, each with the electromotive force e and the internal resistance r_i, and if the circuit is completed by another resistance r_a, then $i = \dfrac{ne}{nr_i + r_a}$. If

r_i is small, as in the case of an accumulator, and r_a great, then i is n times as great as with a single element. If r_a is small compared with r_i, i is equal to $\frac{e}{r_i}$, and no advantage is obtained by the use of several cells. If, however, the cells are arranged in series, that is to say all the positive poles joined to one end of the resistance r_a, and all the negative poles to the other, an element is obtained of electromotive force e, but the cross section is increased n times, and i becomes equal to $\frac{e}{r_a + \frac{r_i}{n}}$; hence when r_a is small, compared with $\frac{r_i}{n}$, $i = \frac{ne}{r_i}$. This case, however, occurs very seldom in work with solutions.

Resistances are chosen of such materials that the specific resistance is relatively high, and does not vary too greatly with temperature; then the resistances do not change appreciably for variations of room temperature, or for the heat developed by the passage of current. Examples of such materials, which are usually made from copper and nickel, are "constantan," "nickelin," and "manganin." They are rather easily oxidisable.

Prepared resistances are wound usually as follows; the number of ohms in one metre of wire are measured, and the corresponding length rolled (preferably by means of a turning lathe), round a cotton spool or a cork; the clean ends are soldered to two insulated wires stuck into the cork and the whole insulated with sealing-wax.

The most convenient form of adjustable resistances is that manufactured by Ruhstrat at Göttingen. The wire—of thickness depending on the magnitude of the desired resistance—is half sunk in the screw thread of an insulating slate bed. The ends are connected to binding screws, to one of which is joined a thick knob of brass of negligible resistance, over which a slide moves, and thus makes contact with one end of the wire; the slide should also carry a binding screw, which can be used as a handle.

Accurate resistances are always fitted into boxes. They each lie between two brass slabs, and are inserted in a circuit by pushing a conical brass key (provided with a small ebonite handle) tightly into the conical opening between the two slabs. The ground surface of the key must not be rubbed with the fingers or laid on any but a clean surface. All traces of grease, oxide, or sulphide on the key are removed by rubbing it with a piece of leather or a linen rag dipped in a little petroleum.* If necessary very fine emery paper is used.

Any dust which has accumulated between or under the brass slabs is removed with a hand bellows, and the apparatus dusted with a fine brush. Usually a box contains a large series of resistances. Practically the series is arranged in tens (decade rheostat). 1, 2, 3, 4 Ω lie in one row next to one another and form the first decade, 10, 20, 30, 40 Ω the second, and so on. Between every two resistances is placed a screw connection (or a hole into which a screw connection ending in a cone fits) by means of which the resistance is inserted into the circuit. Each decade is connected with the next by means of a thick bent hoop, which is held by screws and can be removed, so that each can be inserted separately. In this way complicated arrangements can be built up with a single resistance box, *e.g.*, resistance in current circuit, a part of the resistance joined to a galvanometer (galvanometer in shunt), and the largest resistance joined with the measuring instrument as ballast.

With plugs arranged next to one another, if one is extracted its neighbour easily becomes loosened. Hence in every case all the plugs must be gripped slightly with the forefinger to see whether they are fixed firmly. After use they should all be loosened.

Accurate commercial resistances are quite reliable throughout, and for most purposes the so-called technical resistances of approved firms are sufficiently good.

Wires which are wound continuously will exercise an external magnetic effect when a current is passed through them, and on closing and breaking the circuit they produce an oppositely directed electromotive force (self-induction).

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* According to Werner Siemens, metal without petroleum is an insulator.

The wires are therefore bent in the middle and wound in the *bifilar* form. Then the effect of the current neutralises itself in two neighbouring wires, since there is a current flowing in each of two opposite directions. Larger bifilar wound resistances ($> 1000\,\Omega$) do not give good results with alternating currents, since their electrostatic capacity becomes too great. The wires are in this case, according to Chaperon's method, wound alternately unifilar, and in this way resistances are obtained which can be used for direct and for alternate currents.

Contacts and Connections.

In order to avoid resistances at junctions care must be taken that the contacts are good. All ends of wires, binding screws, etc., must show a bright metallic surface, and must be cleaned with knife, file, or emery paper. The twisting together of two wire-ends or of wire and screw connections is not sufficient. Binding screws must be used which can exert a strong pressure. Pieces which remain in continued contact should be soldered with tin-solder, but the solder liquid must be removed completely. As connections are used silk-covered copper wires, and for stronger currents well insulated cable. If a copper wire is to be fastened to a constantan resistance care must be taken that the junction is not warmed by the heat from the hand or some other source. Every degree rise of temperature produces a thermo-potential of 0·00004 volt, which can cause an error in accurate measurements.

Long wires are always twisted spirally so that they are elastic and can be easily lengthened or shortened. In fastening a wire to a binding screw care must be taken that the wire is so placed between the screw and its base that on tightening the screw the wire is not forced out but drawn in and held more firmly.

Mercury cups only give certain contact when the mercury is pure, and the metal which dips into it is clean, and where possible amalgamated. If neither is the case the immersed wire may become covered by a dirty sac which gives quite uncertain contact.

A block of paraffin in which 1 cm. deep holes are bored with a knife, a little pure mercury and some stout pure copper wire are the materials from which are constructed the simplest and best current breakers, reversers, etc. An often used form is shown in the accompanying figure (Fig. 35). *P* is a paraffin block with six holes; 3 is joined with 6, 4 with 5, and into 1 and 2 dip the current connections. Two stout copper wires are joined to the insulated handle *H*, and so bent that while an end of each dips into 1 and 2 respectively, other ends dip either into 5 and 6 or 3 and 4 respectively, and in this way the current passes in one or the other direction. If 5 and 6 are joined to the connections of a second circuit, and the cross wires are removed, then the current can be passed through one or the other circuit alternately.

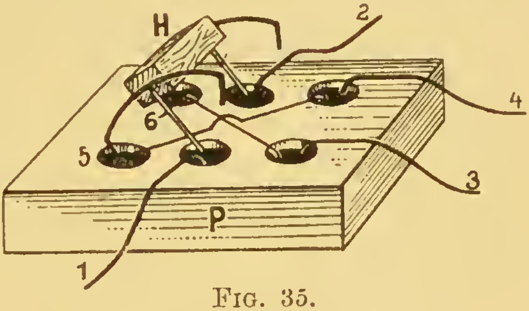

FIG. 35.

Sources of Current.

Lead accumulators are used chiefly as sources of current; when exhausted they can again become charged. They consist of the cell Pb,H_2SO_4 (of specific gravity 1·18—1·23), PbO_2. To obtain more current, more ampere-hours, several Pb – and PbO_2 – electrodes are generally placed in the same solution. Freshly charged accumulators may have a potential of 2·5 volts. The potential falls rapidly with use and remains a long time constant at just over 2 volts. The potential should not be allowed to fall below 1·83 volts, so that it must be tested from time to time, for which purpose a handy and quite exact commercial instrument has been devised (the *accumulator tester*). The plates of the accumulator must always be covered with acid. Therefore it is when necessary filled up with water or accumulator acid. The acid should contain no platinum. The accumulator is damaged both by rapid discharge and by remaining long in an uncharged condition. It is contained best in a simple wooden stand or box, and the poles soldered once and for all to two binding screws, marked + and −, which are arranged on opposite sides of the wooden case. Further details connected with the use of accumulators will be found in the small special treatises of Dolezalek or Elbs.

If a smaller potential is required, which need not be constant, the so-called dry cells are recommended (Zn, sawdust or kieselguhr soaked with NH_4Cl, and charcoal—manganese dioxide). Their internal resistance is naturally not a negligible quantity, whilst that of the accumulator is a minimum (large electrodes, fixed very close to one another in a strongly conducting solution).

The *normal elements* (pp. 152, 153) are *never* to be used as sources of current, but only in circumstances where practically no current passes, consequently where the circuit contains a very large resistance or where their potential is balanced by an equally great and oppositely directed potential. At a maximum the current which could be obtained from them is only $\frac{1}{10000}$ to $\frac{1}{20000}$ ampere. Their internal resistance is very great and must *never* be neglected.

If alternating currents are used the smallest form of induction coil with a platinum contact breaker is sufficient in almost all cases. It can be driven by a single cell, and even then a small resistance must be included. The resistance and the contact breaker are so arranged that a feeble, as shrill as possible, tone is produced (the buzz of a gnat).

Measuring Instruments.

Since the construction and method of use varies with each type of instrument, only the principles common to the most important forms of apparatus can be dealt with. With respect to all details the larger physics books must be consulted, or perhaps the easily accessible special catalogues of the different manufacturing firms.

The principle which especially comes into consideration in such instruments is shortly as follows: A small magnet-needle is placed inside one, or between two coils of wire; when not deflected it is parallel to the plane of winding of the coils. When a current is passed through the coils the needle is deflected. For small deflections the angle (apart from the consideration of other variables) is proportional to the current strength, and inversely proportional to the torsion of the needle suspension (needle galvanometer). In more recent instruments a fixed, relatively strong magnet is used and an easily movable wire coil, through which passes the current which is to be measured (suspended coil galvanometer). In the position of rest the plane of winding of the movable coil and the magnetic lines of force coincide.

The use of a strong magnet in this construction prevents errors arising from other magnetic influences, and in that way the sensitiveness is at the same time increased. The torsion force of the suspension (which depends directly on the current) is made as small as possible by the use of a very fine-drawn suspension wire, *e.g.* of platinum. Good mirror galvanometers are provided with exchangeable coils of different sensibilities. The resistance of the instrument is known always, so that resistances can be inserted in suitable ways in parallel or in series.

In the coil swinging in the magnetic field an induction current arises, which damps the swings. The damping is inversely proportional to the total resistance; it should not be made too great, or else the galvanometer "crawls," comes to rest very slowly.

If the damping is too slight so that the cessations are not aperiodic, a resistance must be inserted in series, whereby the sensitiveness of the instrument is diminished (Fig. 34). A distinction is drawn between mirror and needle galvanometers. In the case of the former the movable system carries a small light mirror, whose deviation is measured by Poggendorff's method.

Telescope with scale. Reading of the scale divisions, which are visible on the cross thread of the telescope. Measurement with and without passage of current. Proportionality of deviation and mirror reading only with small angles.

In needle galvanometers, which are much more convenient, but less sensitive, the needle joined to the movable system moves over a scale, which is divided either into arbitrary parts or into definite units (ampere, milliampere, volt). To avoid errors of parallax the needle end is knife shaped, and sharp pointed, and the needle moves backwards and forwards over a mirror fixed beneath. The connection with the current is made, in the best instruments, by means of two fine spirals, which give conjointly a propulsion to the movable system and draw it back to zero position when no current is passing. All the best instruments have binding screws, screw supports, zero point corrections, and arrestments. The system only hangs freely when the screw supports are accurately adjusted for a horizontal position. After use the needle is arrested.

The deflection in any instrument is proportional to the current intensity; the instruments are therefore, above all, amperemeters. If, however, the instrument has such a large resistance R, that the remaining resistance in the circuit need not be considered in comparison with it, the deflection is proportional to the potential, and the reading is converted into volts, according to the principle $e = i \times R$.

Such an instrument is joined best in a side circuit, since then the current intensity in the main circuit is scarcely altered (see p. 116). The typical arrangement is: amperemeter in main circuit, voltmeter in side circuit.

In working with alternating currents, only null instruments can be used for these purposes, *i.e.*, instruments which show when no current is passing. Galvanometers cannot be used with alternating currents. They are replaced by the telephone, which is silent for direct currents (except when opening or closing the circuit).

Exercises.

Arrange in circuit an accumulator or a dry cell, a simple plug rheostat or a Ruhstrat resistance, and a cheap galvanometer, and convince yourself that the formulæ given are correct.

If, *e.g.*, two accumulator testers with different internal resistances are available, show that with a dry element two different E.M.F.'s are obtained, both a little too small, since the internal resistance of the cell is not taken into consideration compared with that of the voltmeter resistance. Calculate the E.M.F. and R_i from R_{a1}, and R_{a2} and the two deflections. Observe also that for an accumulator equal potentials are obtained with the two instruments.

Increase the range of a galvanometer and an amperemeter; measure the potential and current intensity with potentiometer in a side circuit; insert two resistances in series and parallel respectively.

Determine the heat equivalent of 1 volt-ampere-second by passing a current of known strength and known potential for a measured time through nickelin or manganin wire, insulated by means of sealing-wax, soldered to thick copper wire, and immersed in a small calorimeter (wire resistance 10 Ω, three accumulators in series, current passed for about 2 minutes, 200 grams of water in the calorimeter). The wire resistance must be measured, if unknown (see above), and a voltmeter joined to its ends so that i can be calculated according to Ohm's Law. In practice the arrangement is usually inverted, and the calorimeter calibrated by these means.

Capillary Electrometer.

The **capillary electrometer** of Lippmann depends on quite a different principle to the measuring instruments already mentioned. Ostwald has modified it into a convenient and cheap laboratory instrument, which is exclusively employed as a null instrument. In a sloping or vertical capillary, a movable mercury thread is connected with a large mercury meniscus by means of 25 per cent. sulphuric acid. The position of rest is given at the meniscus by the surface tension and hydrostatic pressure of the mercury column in which the thread ends. Into both mercury reservoirs are dipped platinum wires, which are almost entirely fused into glass tubes so that they do not come into contact with acid. They are connected with the poles of a cell, the mercury in the capillary to the negative pole so that at that point is produced the hydrogen polarisation. In that way the surface tension is diminished, the mercury meniscus moves in the capillary; the displacement can be read by means of a microscope on a scale placed beneath, or, with a vertical capillary, by means of a small power microscope carrying a micrometer scale in the eyepiece. With very small differences of potential, proportionality exists between deflection and polarisation. Readings cannot be made with above 0·95 volt. In the position of rest the two quantities of mercury are joined together, *i.e.* the instrument is "short-circuited."

The surface of contact between mercury and acid must be renewed frequently, for which purpose a drop of mercury is forced out of the capillary. Only the purest mercury (preferably shaken up with potassium bichromate solution) is suitable for the instrument. The form with vertical capillary is shown in Fig. 36.

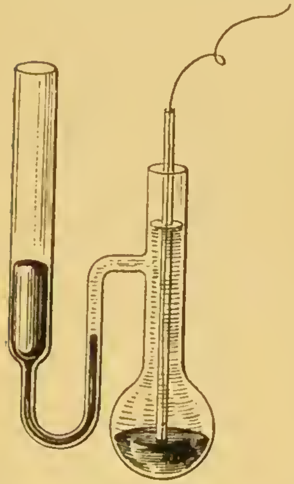
FIG. 36.

The instrument must form a closed circuit, except at the moment of use. This is accomplished by means of a simple key with three binding screws (see Fig. 37). A thin flexible strip of brass is screwed to a small stand of wood soaked in paraffin by means of a binding screw *A*. In a position of rest the brass strip rests beneath a second fixed strip, at right angles, and joined to the binding screw *B*. The electrometer connections are joined to *A* and *B* respectively. The flexible brass strip carries an ebonite or vulcanite knob at its free end. When the knob is depressed, *A* is no longer connected with *B*, but with a third fixed brass strip, which is connected with the binding screw *C*. The E.M.F. which is to be measured is joined to *B* and *C*. Poggendorff's compensation arrangement is usually employed with this instrument (cp. Fig. 44, and pp. 155 and 156); the key and electrometer are substituted for the galvanometer *G*, and its ballast resistance *R*.

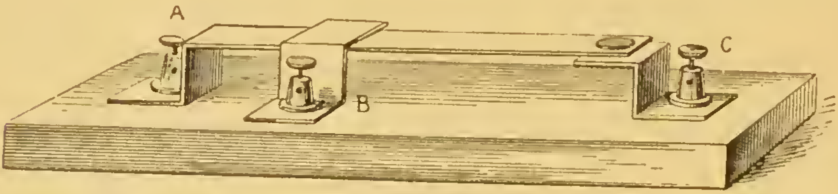

FIG. 37.

An example of the use of the capillary electrometer is given later (see p. 163).

CHAPTER IX

ELECTRICAL CONDUCTIVITY

General Remarks.

The Wheatstone's bridge arrangement is most suitable for the measurement of conductivities; it consists of six current branches. Four resistances, X, R, b and a, are arranged in a circuit; the source of current E is inserted between $X-R$ and $a-b$, and the zero instrument T between $X-a$ and $R-b$ (see Fig. 38). E is the only source of potential in the system. From the laws, already stated, for a current which is conducted through two paths, it follows that no current flows through T only when $\frac{X}{a} = \frac{R}{b}$. Hence

$$X = R\frac{a}{b}.$$

The measurements of a and b are reduced to measurements of length; for this purpose a homogeneous calibrated wire is taken and stretched on an insulating stand. A contact connection slides along it, and thus divides it into two parts a and b. From p. 113 it follows that if the cross section and the specific conductivity of a wire are the same throughout, then $\frac{R_1}{R_2} = \frac{l_1}{l_2}$. R is a variable resistance (such as an ordinary resistance box).

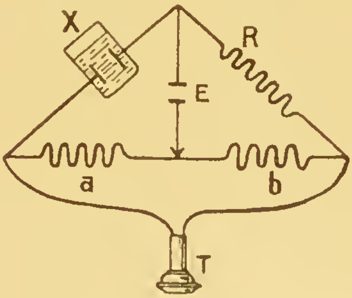

Fig. 38.

If the resistance of a wire is measured, an accumulator or a dry cell E is taken as source of the current, and a galvanometer as the zero instrument. If the resistance of a column of liquid has to be determined, in which conduction of current is accompanied by electrolysis, an alternating current must be used, with which every reversal of current compensates the decomposition effect due to the previous one. In this case E is the secondary of a small induction coil, T a telephone.

Suitable forms of apparatus are constructed to measure the resistance of wires, in which R, a and b are built into a resistance box, to which X, E and T are connected. Both a and b can be altered to 1, 10, 100, or 1000 ohms, so that the ratio of $\frac{a}{b}$ can be varied between $\frac{1}{1000}$ and $\frac{1000}{1}$; X, the unknown resistance, can then always be found by multiplying by some power of 10. R is a complete resistance box. The apparatus has a double key; when the knob of the key is depressed, the cell and the galvanometer are connected to the circuit one after the other. The galvanometer is protected by previously inserting a very large resistance, which can be cut out by pressing down the second key, in cases when the deflection of the galvanometer is made very slight.

If the student does not understand the arrangement, the apparatus should be constructed with a less delicate galvanometer (one used for purposes of demonstration) and single resistances.

The physical chemist is concerned with the resistance of wires merely as serviceable magnitudes.

Conductivity of Solutions.

The electrodes consist of platinised platinum; in the case of solutions which are easily decomposed, or so dilute that the concentration would be altered considerably by oxidation or slight adsorption by the platinum black, ordinary platinum electrodes are used. Platinising reduces the polarisation at the electrodes, and thereby improves the minimum of the telephone.

Before the electrodes are platinised they are cleaned thoroughly (with chromic acid mixture, nitric acid, or sodium hydroxide, according to the nature of the deposit), and washed with distilled water.

The best platinising solution consists of 1 gram $H_2 PtCl_6$ and 8 mgs. of lead acetate dissolved in 30 grams of water. It becomes more dilute in use. The actual platinising is carried out with the current from two accumulators; the direction of current must be reversed frequently, and the amount regulated so that a moderate production of gas results. After the liquid has been poured away and the electrodes rinsed with water, the vessel containing them is filled with sodium acetate solution, and this electrolysed for a short time, reversing the current frequently as before; in this way the products of decomposition of the first solution are gradually removed from the platinum black. The electrodes are finally washed with warm water by decantation, and the warm water renewed continually until its conductivity no longer changes.

Since the specific conductivity $\kappa = \frac{l}{q} \times \frac{1}{r}$, both the distance between the electrodes l, and their cross section q must

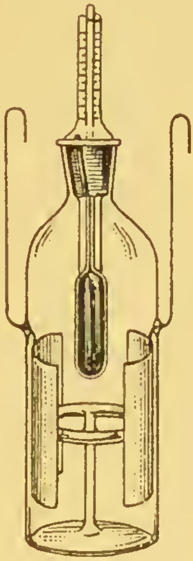

Fig. 39.

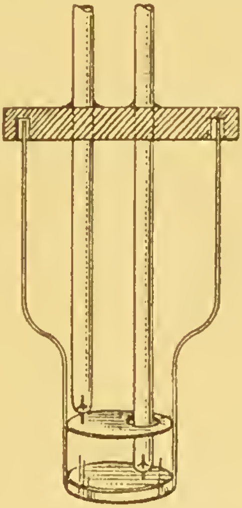

Fig. 40.

be accurately fixed. Hence—from motives of false economy—too thin platinum foil must not be used for the electrodes. $\frac{l}{q}$ is termed the *resistance capacity* of the vessel. A distinction is drawn between **conductivity vessels** with constant and with variable resistances. Of the numerous types which have been proposed, the following are employed chiefly.

A. *Kohlrausch's Type* (Fig. 39). The electrodes are fused through the side of the vessel. The bent upper ends of the platinum wires dip into mercury cups. The lower ends are insulated with a covering of thin indiarubber tubing; they are cemented to the vessel walls with rosin at their point of fusion, in order to increase the stability. The electrodes are kept in position by pressure against a small glass ring joined to the bottom of the vessel. The cell must not be dried; it is kept filled with distilled water (as are all the other types), and before use is rinsed several times with the solution to be investigated. A groove should be filed in the opening for the thermometer, so that the air can escape when it is inserted. $\frac{l}{q}$ is generally about 0·2, and is not quite independent of the height of the contents. In consequence it must always be filled to the same height (to a ring of shellac varnish).

B. *Ostwald's Type* (Fig. 40). The electrodes are fused into glass tubes by short platinum wires; the tubes are cemented into a vulcanite lid. The current connections are effected by means of copper wires and mercury. The electrodes fill the lower section of the glass vessel almost completely, so that the resistance capacity is almost independent of the height of the contents, since scarcely any of the current is carried by the liquid in the upper part of the vessel.*

The greatest care must be exercised in removing the lid so that the electrodes are not bent by scraping against the glass wall. The lid contains an opening for a thermometer. The capacity of the vessel is essentially of the order of magnitude 0·5.

Other forms of vessel have been designed for liquids which are either specially good or specially bad conductors; these will be found in the classic handbook of Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*, Leipzig, 1898.

Forms of apparatus with variable resistance capacity, having movable electrodes, possess the disadvantage that the capacity is subject to unintentional alterations.

Although the following form cannot be varied continuously, yet it can be altered step by step sufficiently, and has a reliable steady capacity. With a rather large quantity of liquid the amount of platinum required is small, and the capacity depends but slightly on the height of the contents. The design is the *Nernst-Magnus* type (Fig. 41).

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* This is seen in platinising the electrodes; the upper surface of the upper electrode is scarcely tarnished.

C. A stout glass vessel is closed by a tight fitting ebonite lid, which contains four openings, two small ones for the stirrer and thermometer (not shown in the figure) and two larger, the sizes of which are perceptibly different. Two ebonite collars fit into these openings and are held in position by projecting rims. From the edge of each of these a segment is cut off, and the flat edges of the two rims press together when the rings are in position, so that they are held firmly in place. A glass tube is cemented into each collar. Since the widths are different, two sizes of tubes are employed and two of each kind taken. One pair has the lower openings drawn out and narrowed, while the upper are of equal width. These are closed with ebonite stoppers; through them are cemented glass tubes which support the electrodes beneath. The stoppers also possess projecting rims, of which corresponding sections are cut off, and when fitted together hold the tube firmly in one position. The electrodes fill the cross section of the tube almost completely (Fig. 41a).

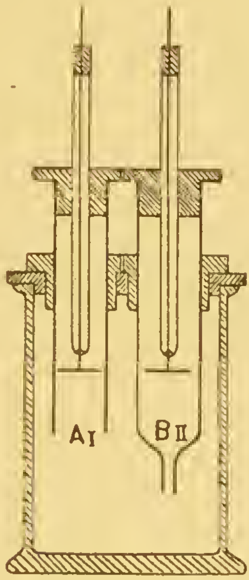

FIG. 41.

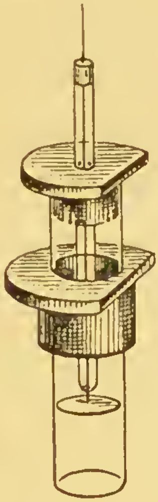

FIG. 41*a*.

Thus with four tubes, but only two electrodes, four definitely fixed capacities are obtained; these can be arranged suitably according to the nature of their openings (A_IB_I, A_IB_{II}, $A_{II}B_I$, $A_{II}B_{II}$). Any two of them when put together possess a constant capacity since the positions are fixed. Capacity, however, does vary slightly with height of liquid content. The vessel is, in consequence, always filled to a definite mark, which represents a convenient volume, about 100 c.c.

Kohlrausch has constructed a very convenient vessel for the analysis of strongly conducting solutions; in the use of this vessel a stretched wire resistance is unnecessary. It is U-shaped, of small cross section; it has well platinised electrodes arranged horizontally, fitted to two corks, by which means they can be moved vertically. It carries on each side a scale from which the resistance capacity can be determined in any position. Two equal resistances are taken for a and b, so that the telephone is silent when $X = R$. For R such a resistance is chosen that the calculation is simple, and the electrodes are adjusted until the telephone is silent. The scale readings on each side are added, and the capacity thus found. If this is divided by R the value for κ is obtained directly. Since different adjustments of the electrodes will give the same capacity, the scale and reading errors can be corrected by taking several observations in different positions.

Since most of the conductivity vessels can only be dried with difficulty (for heating is dangerous, and alcohol becomes oxidised by the platinum black), they should always be rinsed twice, previous to use, with small quantities of the solution with which they are to be filled.

In all measurements of the conductivity of electrolytes great stress must be laid on accurate measurement of the temperature. For each rise in temperature of 1° the conductivity increases by from 1·5 to 2·5 per cent. according to the mobility of the ions. The most mobile ions ($H^{\cdot}$ and OH') have the smallest temperature coefficients. In making a series of measurements at a particular temperature a thermostat must be used.

After use the vessel must be emptied and washed out several times with distilled water by decantation; the platinum black always absorbs a little of the solute, which is only slowly given up by diffusion.

With solutions which conduct well it is necessary to consider the resistance of the connection wires, which is usually of the order of magnitude 0·05 to 0·10 ohms; (it is measured by filling the dried vessel with mercury, preferably before platinising). With solutions which conduct badly, the **conductivity of the solvent** becomes a factor. Good "distilled" water has at 18° a conductivity of 1 to 2×10^{-6}. (The conductivity depends chiefly on dissolved carbon dioxide, not on the ions of water themselves; really pure water at 18° has a conductivity of only $0 \cdot 04 \times 10^{-6}$.) A neutral salt solution $\frac{1}{1000}$ *n* has at 18° a conductivity of about 110×10^{-6}, which is consequently only from 50 to 100 times as great as that of the solvent; with a weak acid, as acetic acid, the corresponding ratio is only 20—40 : 1.

According to the law of mass action the dissociation of carbon-dioxide dissolved in water is completely prevented by the presence of larger amounts of other acids, so that the conductivity of water is not subtracted from the observed conductivity of acid solutions, always assuming that it is so small that it is really derived from carbon-dioxide and not from salts. The conductivity of water is subtracted in the case of salt solutions if it is not less than the error of measurement. The conductivity vessel should be made of Jena glass if possible (Glass 16 III., or 59 III.). It is always kept filled with water, which should be occasionally renewed even when the vessel is not in use. In this way the amount of alkali dissolved from the glass is diminished during a measurement; such action frequently takes place with new vessels, and may give false results in work with acids.

The most convenient resistances are from 50 to 1000 ohms. Pieces of more than 1000 ohms must be wound according to Chaperon's method (see p. 120).

Unnecessarily strong currents must be avoided, nor should current be passed longer than necessary, since the heat produced might affect the result.

In the determination of *a* and *b* with a stretched wire a length of one metre cannot well be exceeded. The accuracy of measurement is increased considerably by using a much longer wire wound spirally ten times round a cylindrical drum on insulating material.

The Cylinder Bridge.

The cylinder is divided into 100 parts, and a fixed pointer indicates the reading. A metal axis arranged parallel with and in front of the cylinder, and which is divided into 10 parts, carries a little contact wheel which slides along the cylinder and is pressed against the measurement wire by a spring.

The groove of the wheel and the axis itself must be kept perfectly clean. In more elaborate types of instrument a few ordinary resistances are built into the stand for the sake of comparison (generally 1, 10, 100, 1000, and 10000 ohms). However, an ordinary resistance box, which allows closer comparison, is almost preferable.

If in very accurate work the same range of the measurement wire cannot always be used, the wire must be calibrated (for further details see larger text-books). By a series of double measurements (first arrangement $X - R$, second $R - X$) corresponding to double weighing, in which the mean result is taken, any lack of symmetry of the wire can be eliminated. The accuracy of measurement can be increased by inserting before the measuring wire suitable multiples of its resistance.* The middle of the bridge is used as much as possible. A rough or a mathematically precise reckoning (see p. 6) will show that the same error of position affects the result least when the reading is in the middle of the wire. If a complete box of resistances is used, it is always possible to make $a = b$ unless the unknown resistance X is very large, as when measuring water, or very small, as in the case of wire resistances. But in both of these cases no great accuracy is required, since the results themselves are used only as corrections.

The telephone should give a soft high sound; it should be pressed firmly to one ear, and the other closed by means of a small glass bulb with wide neck (an antiphone).

If, as the contact wheel slides along the wire, no definite position of minimum sound is obtained, two positions are determined at which the sound is equal, and the mid-point taken, or the method is adopted which is used in the half-shadow apparatus (see p. 85).

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* *E.g.*, if the resistance of the wire is 10 Ω its accuracy will be considerably increased if 10 Ω are inserted on each side of the wire, in the same circuit.

If the minimum is uncertain on account of electrical (or electrostatical) changes in the resistance spools or the vessel, another branch of the circuit of equal capacity is arranged in parallel; it contains a small plug condenser, and the arrangement which gives the best minimum is found by trial (cp. the chapter on electrostatics).

The induction coil should always be removed as far as possible from the cylinder bridge, so that the lines of force from the coil may not disturb the telephone. For the same reason the axis of the coil should be arranged at right angles to that of the bridge.

The **resistance capacity or cell constant** $\frac{l}{q}$ can be determined by a length measurement only in the simplest form of vessel. Kohlrausch has accurately calibrated a long cylindrical vessel containing electrodes, which completely filled its cross section, and with the resistance capacities thus found has determined *absolutely* the conductivities of a series of **standard solutions** at different temperatures. These can be easily and accurately reproduced, and employed to calibrate vessels whose resistance capacity cannot be measured directly.

A selection of such solutions is given.

Temp.	Saturated NaCl Solution. κ	1 n KCl Solution. κ	$\frac{1}{10}$ n KCl Solution. κ	$\frac{1}{50}$ n KCl Solution. κ
15°	0·2014	0·09252	0·01048	0·002243
18°	0·2160	0·09822	0·01119	0·002397
20°	0·2259	0·10207	0·01167	0·002501
25°	0·2513	0·11180	0·01288	0·002765

It is seen from this table that the molecular conductivity of KCl increases rapidly between 1n and 0·02n, and further that the temperature coefficient $\left(\frac{\kappa_{t_1} - \kappa_{t_2}}{(t_1 - t_2)\ \kappa_{18}}\right)$ amounts to about 2 per cent.

Linear interpolations can always be made. It is of course taken for granted that the above conductivities are the observed values less those for the conductivity of water. A normal solution of KCl is prepared by weighing out 74·55 grams of pure dry KCl, and dissolving it at 18° to a (true) litre of solution.

Exercises.

1. The Absolute Measurement of Conductivity.

A cylindrical glass tube, about 15 to 20 mm. internal diameter and 15 cm. in length, is fixed vertically, and closed at each end by a rubber cork, through which are thrust thick platinum wires. These carry horizontal circular plates of platinised platinum black, which completely fill the cross section of the tube.

The tube is filled with tenth normal KCl solution. In inserting the upper rubber cork, in order to prevent any air bubbles being enclosed, a thin wire is also pushed into the tube, the cork squeezed in until all air bubbles are pressed out from below the electrodes, and the wire then cautiously withdrawn.

The vessel is closed tightly and allowed to remain for a short time until it reaches room temperature (measured on a thermometer hung near it); it is measured against three different wire resistances. The resistances are so chosen that the readings are made near the centre of the cylinder wire; three readings are taken with each wire resistance. $R\frac{a}{b}$ is calculated for each resistance. After the thermometer has been read, l is measured at four positions of the tube with a good ruler (perhaps a slide rule). The diameter is measured with a caliper or other accurate instrument, and κ calculated from $\kappa = \frac{l}{qr}$.

The mean cross section of the tube can also be measured by weighing it filled with water. In this case the length between the two corks must be measured.

With accurate work, the value found should agree with that calculated from the table to within about 1 per cent.

2. Measurement of the Resistance Capacity of a Vessel (Cell Constant).

The vessels of the Kohlrausch, Ostwald, Nernst-Magnus, and similar types, should be calibrated with one or other of the normal solutions.

Measure the maximum and minimum capacities of the Nernst-Magnus cell; these measurements need not be carried out at any particular temperature, since the normal solutions have been measured accurately between 0° and about 35°. The actual temperature of measurement must be accurately determined.

3. Molecular Conductivity of Salts.

A solution of NaCl or KCl is prepared of approximately the concentration used in measuring the depression of freezing point or elevation of boiling point; the specific conductivity is measured at 18° or 25°, and the molecular conductivity, Λ calculated,

$$\frac{\kappa \times 1000}{n} = \Lambda.$$

At 18° Λ_∞ for NaCl is about 109, for KCl about 130, at 25° about 127 and 150 respectively. $\frac{\Lambda}{\Lambda_\infty}$ must be approximately equal to the degree of dissociation previously determined by osmotic methods (see p. 41).

4. Determination of the Dissociation Constant of Malonic Acid.

From the law of mass action it follows that for binary electrolytes $\frac{\text{(concentration of ions)}^2}{\text{concentration of undissociated molecule}} = \text{const.}$ (see p. 100).

If v is the reciprocal normality, and in consequence the number of litres in which a gram-molecule of substance is dissolved, then $\frac{\Lambda}{\Lambda_\infty v}\left(\text{or } \frac{1000\,\kappa}{\Lambda_\infty}\right)$ is equal to the ionic concentration $\left(\frac{1}{v} - \frac{\Lambda}{\Lambda_\infty v}\right)$, equal to the concentration of the undissociated molecule. Hence $\frac{\Lambda^2}{\Lambda_\infty(\Lambda_\infty - \Lambda)v}$ = constant = the *dissociation constant.*

Dibasic organic acids dissociate into two ions only, H and AcH, so long as the degree of dissociation remains below 50 per cent. The formula given can therefore be used for not too dilute solutions of dibasic acids.

Determinations are made for a series of concentrations which can be altered by the following method: The solution in the cell is diluted by pipetting out half the contents, and pipetting in an equal volume of water at the same temperature. To be able to do this a definite volume of solution must have been pipetted into the dried vessel originally. Two pipettes are needed; the one allows the *same quantity* of liquid to *flow out*, as is *sucked up* into the other (standardised for outflow and inflow respectively). The measurements are made more accurately, if there is sufficient acid at disposal, by diluting the solution in a flask at the temperature of measurement, and rinsing out the vessel with solution before every measurement. Or the acid is weighed out and added to a known volume of water in the conductivity cell; in order that this method can be employed the acid must be easily and quickly soluble.

Malonic acid is a very suitable substance.

The Nernst-Magnus cell is dried with a clean cloth and a piece of blotting paper, which is applied to the edges of the electrodes; the widest tubes are employed, and 100 c.c. of good conductivity water pipetted in. Enough solid malonic acid is weighed out to give a concentration of about $\frac{1}{400}$ *n*. Since only about 25 mg. are required, they must be weighed with great accuracy. After the acid has dissolved the resistance is measured. An equal amount of acid is weighed out and a fresh measurement made. Finally, about 50 mg. are weighed out and added and a final reading taken. In this way three solutions are obtained for which v is approximately 400, 200, and 100.

All three measurements must be carried out at the same temperature. The three values of Λ are calculated.

Successive values are roughly in the proportion of $1{\cdot}4 = \sqrt{2}$. If, as is not quite the case here, Λ is small compared with Λ_∞, it follows that—

$$\frac{\Lambda_1{}^2}{\Lambda_\infty{}^2\, v_1} = \frac{\Lambda_2{}^2}{\Lambda_\infty{}^2\, 2\, v_1}, \text{ whence } \frac{\Lambda_2}{\Lambda_1} = \sqrt{2}.$$

Compare with this result Ostwald's values for weaker acids. *E.g.*, for acetic acid at 25° $\Lambda_8 = 4{\cdot}63$, $\Lambda_{16} = 6{\cdot}50$, $\Lambda_{32} = 9{\cdot}2$, $\Lambda_{64} = 12{\cdot}9$, $\Lambda_{128} = 18{\cdot}1$, etc.

For an acid with 11 atoms at 25° Λ_∞ is 388, the temperature coefficient 1·5 per cent. per degree. Λ_∞ cannot be measured for malonic acid, even though accurate measurements could be made at infinite dilution, since even with a $\frac{1}{400}$ *n* solution the acid is perceptibly dissociated into three ions. In such a case Λ_∞ can only be found by analogy. Ostwald has shown that the mobility of organic anions which consist of somewhat large complexes of atoms depends only on the number of atoms. For an anion of 10 atoms at 25° v is about 43, $u_{\mathrm{H}^\cdot} = 345$.

The dissociation constant should be calculated for the solutions whose resistances have been measured. With accurate work a good constant will be obtained for the more concentrated solutions (about 0·0015), but for the dilute solution a somewhat greater value, since already $\frac{\Lambda}{\Lambda_\infty}$ is > 0·5, and dissociation into three ions is perceptible.

Frequently the values given (K) are 100 times those for the dissociation constant, and are calculated from the formula $\frac{a^2}{(1 - a)\, v}$; the degree of dissociation a is reckoned in percentages.

Remarks.—If two reliable determinations of K are compared, which have been calculated from experiments carried out at considerably different temperatures, the figure corresponding to the higher temperature will be somewhat greater; the values can be used to calculate the heat of dissociation q (about 1000 g. cal. per molecule of malonic acid).

$$\ln \frac{K_2}{K_1} = \frac{-q}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

(cp. pp. 2 and 61).

The measurement of conductivity has become a largely used **analytical method**: it is indispensable for very dilute solutions where chemical methods of analyses fail (cp. Kohlrausch and

Holborn). The method is applicable to all salts, whereas the second electrochemical method of analysis, the measurement of the E.M.F. of concentration cells, although also applicable to very dilute solutions, can only be used for a metallic salt with electrodes made from the same metal, or of which the anion forms a practically insoluble compound with a convenient electrode metal (see concentration cells, p. 158). The values given on p. 59 for the solubility of AgCl are calculated from the conductivity values.

5. Solubility of a difficultly Soluble Salt. Decrease of Solubility and Dissociation. Example $PbSO_4$ — H_2SO_4.

The conductivity of distilled water at 18° is measured in a Kohlrausch's resistance cell. For this purpose the contents must be renewed until a constant value is obtained. When this is reached, some thoroughly washed lead sulphate is added to the final water contents, the whole shaken up, and the conductivity measured. The solution is quickly saturated. Measurements are made after shaking up and after the solid has settled until constant results are obtained.

Let κ be the conductivity of the saturated solution after that of water has been subtracted (about 32×10^{-6}), and $\Lambda_\infty = 61 + 68$, the final conductivity of a gram equivalent of $PbSO_4$ ($= \frac{1}{2}PbSO_4$), then the equivalent normality of the saturated solution is, if we assume complete dissociation,

$$n = \frac{1000\,\kappa}{129};$$

the number of gram-molecules in the litre is half as great.

If the same experiment is made, replacing water by a $\frac{1}{50}\,n$ to $\frac{1}{100}\,n$ solution of H_2SO_4, then very little of the $PbSO_4$ is dissolved (decrease of solubility) and the change of conductivity is very slight. With still more dilute H_2SO_4, addition of $PbSO_4$ results in a slight decrease of conductivity. Both electrolytes with the common ion SO_4'' are rather less dissociated in the mixed solution than in pure water (decrease of dissociation). The mobile H ions are replaced to a slight extent by the less mobile Pb ions. Hence there results a decrease of conductivity, which, however, is very small in consequence of the small quantity of salt which dissolves.

CHAPTER X

FARADAY'S LAW—TRANSPORT NUMBERS

The Absolute Determination of the Current Intensity.

The absolute value of the current intensity is determined by means of the tangent galvanometer. In the centre of a Ω-shaped piece of copper swings a short magnet-needle, which carries a light aluminium pointer moving over a circular scale. The copper ring is so rotated that the needle (not the pointer, which is at right angles to it) lies in the plane of the coil, and coincides with one of the diameters of the circle. The ring is then in the magnetic meridian and the pointer should be at zero. If a current of intensity I (measured in C.G.S. units) passes through the coil, it will tend to turn the needle through an angle of 90°; since the horizontal intensity of the earth's magnetism exercises a force contrary to that of the current, a deflection of a° (less than 90°) will result. If H is the horizontal intensity, the average radius of the copper circle R cm., the magnetic moment of the needle M, then the force of deflection of the current will be

$$= \frac{I \cdot 2R\pi \,.\, M}{R^2} \cos a = \frac{2I\pi M}{R} \cos a,$$

whilst the moment of the earth's magnetic force will be $MH \sin a$.

In a state of equilibrium

$$\frac{2MI\pi \cos a}{R} = MH \sin a, \text{ whence } I = \frac{HR}{2\pi} \tan a.$$

If the current intensity is reckoned in amperes, this figure must be multiplied by 10 (see p. 110) and there results

$$i = \frac{5HR}{\pi} \tan a.$$

If the copper circle consists of not one, but n windings, then

i must be divided by n. H is approximately 0·18. The exact value depends on geographical position, and to a slight extent on time variations; it can be found in Landolt-Börnstein's tables.

In using the tangent galvanometer the presence of heavy iron masses, such as gas-fittings, iron stands, etc., lessens the value of H; they must therefore be removed. Knives, keys, etc., must be laid aside for a similar reason. R is best determined by measuring several diameters of the coil with a foot rule and taking the mean. The deflection a is read at each end of the pointer. It is advisable to put a commutating key in circuit with the galvanometer alone, so that the direction of the current can be reversed and a new reading taken. In this way the error which results if the ring is not situated exactly in the magnetic meridian is eliminated. The error of reading is smallest when the deflection is about 45°. Since ordinary tangent galvanometers have a copper circle of about 25 cm. diameter, a current of about 4 amperes gives the most favourable deflection. This requires a larger electromotive force than that obtained in most electro-chemical work, so the circle must consist of several windings to obtain the best results.

Faraday's Law.

The following are arranged in a circuit: two accumulators a small variable resistance, a commutator with tangent galvanometer, an ordinary amperemeter, a silver voltameter, and a copper voltameter.

The last two instruments are employed usually to measure the current intensity from its chemical effect, *i.e.*, from the respective deposits of silver and copper. In this case they are used to determine the electrochemical equivalents of silver and copper. Care must be taken that they are arranged in the right order, and they must be tested previously to ascertain which is the cathode and which the anode.

The name *voltameter* is not a very good one; these instruments must not be confounded with *voltmeters*. Recently Richards has suggested the term **coulometer**, which is certainly more appropriate, since in reality *coulombs* are measured.

The **silver coulometer** is constructed best by taking a previously weighed platinum crucible as cathode, a 20—25 per cent. neutral solution of $AgNO_3$ as electrolyte, and a rod of pure silver as anode. The apparatus is put together on the small stands commonly used for electrolytic work (though any small stands will do). As slight disturbances always take place at the anode, especially through formation of higher oxides, small particles frequently fall off. Since the cathode is weighed, to protect it from these small particles, the anode is wrapped up in a small piece of filter paper, or a small basin is placed beneath it. After the current has been interrupted the solution is poured back into the stock bottle; the platinum crucible with the silver deposit is washed carefully by decantation several times with distilled water, until the wash-water no longer gives the silver reaction. The crucible is then left standing for a few minutes filled with warm water, afterwards dried with alcohol, the alcohol evaporated over a flame, and the crucible, when cold, is weighed accurately.

If the current intensity is small, large leaves of silver crystals are formed frequently, and these are easily detached from the crucible. In such cases the washing must be carried out with especial care, and the wash-waters, if necessary, passed through a small filter before they are thrown away. The crucible must be carefully cleaned before use, and immediately after use the silver must be dissolved in nitric acid, and the crucible again cleaned.

The silver coulometer can be used with advantage in standardising the calorimeter electrically, and in the determination of the heat equivalent (see p. 125), since measurements of time and current are dispensed with, and the volt-ampere-second is deduced from the weight of deposit on the crucible and the voltmeter data (readings taken at near intervals).

Experimental Conditions: Calorimeter of 500—600 water equivalent, heat resistance about 60 ohms, time of passage of current seven minutes, potential 10 volts, half minute readings (see p. 125).

The **copper coulometer** is preferably made of a glass vessel similar to those used for accumulators, containing two copper plates insulated from each other, which fill the greater part of the sectional area of the vessel. This is filled with solution so that all but the necks of the plates are covered. The electrolyte is made up as follows: 150 grams of copper sulphate, 50 grams of sulphuric acid, 50 grams of alcohol, to 1000 grams of water. This is the solution recommended first by Öttel; an alternative solution consists of 125 grams copper sulphate, and 50 grams sulphuric acid per litre. Only the cathode is weighed; it is washed with water, and dried first with filter paper, and finally in a vacuum desiccator.

The copper coulometer, like the silver coulometer, is liable to certain sources of error which cannot be wholly avoided. The formation of cuprous ions, whose corresponding equivalent is twice that of cupric ions, is an especial source of error. It can be avoided partly by the use of somewhat concentrated copper sulphate, acidified as previously indicated, to prevent hydrolysis of cuprous salts. Moreover, the solution must be stirred thoroughly to prevent it becoming too weak near the cathode, and air should be driven out of the solution, to prevent oxidation of Cu to $Cu^{\cdot}$. This is accomplished by passing hydrogen or carbon-dioxide through the solution during passage of current. The current density, equal to the number of amperes divided by the area of the electrode, must be kept between 0·02 and 0·002. If this condition is strictly observed, the copper deposit adheres well, is finely crystalline, and light red. In spite of the sources of error, and the numerous conditions to be observed in its use, the copper "voltameter" is almost exclusively used for all technical purposes, since it is more convenient and cheaper than the silver "voltameter," though less exact.

By measuring the time that the current has passed, and the weight of metal deposited, the integral idt is obtained, the number of ampere-seconds; from this the average current intensity is easily calculated. If the current is inconstant, the coulometer permits the determination of average intensity only; to determine the current continuously needle instruments are necessary.

Experiment 1.—See that the connections are in order. Electrolyse the solutions with about 0·7 ampere for 20 minutes, reading the galvanometer every 4 minutes (reversing the current for every reading) and also the amperemeter. Calculate the amounts of copper and silver deposited respectively per second, first from the amperemeter readings, then from those of the galvanometer. (The theoretical figures are 1·118 and 0·3294 mgs. respectively.) The actual figures obtained in all cases, according to Faraday's Law must be in the ratio 107·93 to $\frac{63·6}{2}$.

Experiment 2.—Replace the two coulometers by a resistance of 1 ohm to the ends of which is joined an accumulator tester (range from 0 to 3 volts), which in this way can be used as an amperemeter (for method of correction, see p. 116). Compare the galvanometer, the first amperemeter, and the voltmeter at different current intensities. It will be found that the voltmeter is most exact of the three. With the numbers found with this, correct those obtained in experiment 1. In this experiment only *one* accumulator is necessary.

The Knallgas Coulometer.

For small currents, where metallic coulometers are untrustworthy, the knallgas coulometer is employed. Since under normal conditions 96540 coulombs correspond to $22·41 \times \frac{1·5}{2}$ litres (why $\frac{1·5}{2}$?) one ampere evolves 0·174 c.c. per second, per minute 10·44 c.c. As electrolytes solutions are chosen which give no secondary reaction, such as does H_2SO_4 for example. An approximately 2*n* solution of sodium hydroxide between nickel electrodes is used preferably. A convenient form of this coulometer is shown in Fig. 42. The burette acts as measuring vessel, and displaced liquid is measured instead of gas. Readings are taken before and after passage of current; in each case the surfaces of liquid in coulometer and burette must be at the same level when a reading is made. The barometric pressure must be observed at the same time. The vapour pressure of water over a twice normal soda solution is about 7 per cent. less than above pure water, and this must be taken into consideration (check this statement by a rough calculation according to the theory of p. 57). Before taking the actual measurement, the current should be run for some time, in order to generate enough gas to saturate the electrodes, and especially the solution.

It is assumed that no change of temperature, or only a very slight one, takes place during the passage of the current. Otherwise a correction must be made for the expansion of the gas already present before the commencement of the experiment (this amount can be estimated roughly). Hence the temperature before and after experiment must be noted.

Experiment.—Connect in a circuit two or three accumulators, a convenient resistance, commutating key with tangent galvanometer, amperemeter, and a one-ohm resistance, to the ends of which are connected the terminals of a voltmeter, and electrolyse the solution with about 0·5 ampere until some 50 c.c. of electrolytic gas have been produced. The time must be accurately measured and the current strength read at regular intervals. Calculate the amount of electrolytic gas evolved per ampere-second, and compare the result with the corresponding figures for copper and silver.

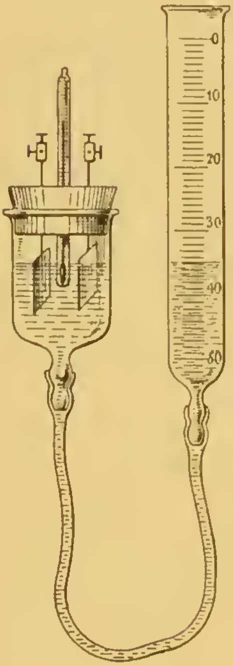


FIG. 42.

Transport Numbers.

When a current passes through an electrolyte of which the cation and anion possess different velocities (u and v), changes of concentration near the electrodes will result. If the change of concentration (not always simple, on account of diffusion and convection) is measured in a suitable vessel, the ratio of the velocities of migration can be calculated. The fraction $\frac{u}{u+v}$, the relative proportion of the current carried by the cation, is called the *transport number* of the cation (Hittorf). For example, if a grams of silver migrate from the anode, in the electrolysis of silver nitrate, while in the same time b grams of silver are deposited in a silver voltameter in the same circuit, it follows that the transport number is

$$\frac{a}{b} = \frac{u}{u + v}.$$

A number of different kinds of apparatus have been suggested to separate conveniently the anode and cathode solutions, and the intermediate unaltered layer, which is also analysed as a check.

A convenient form is that shown in Fig. 43. *A* is the anode vessel; the anode is soldered to a piece of copper wire, and cemented into a bent glass tube with sealing-wax, the tube being thrust through the middle of the cork of the side opening. The copper wire is wholly within the glass tube, and connection with the circuit is made by filling the tube with mercury. The point at which the wire and anode are soldered is protected by a covering of sealing-wax. The anode vessel (an Erlenmeyer flask) holds about 100 c.c. Its upper opening is ground, and can be closed either by a ground stopper or the upper part of the transport vessel (*NL* and *K*). The middle "neutral" layer is contained in *NL*; its concentration will remain unaltered during the passage of the current. The lower end is ground inside as well as outside, the inside being shut by means of a ground stopper to which is fixed a handle, so that it can be raised during electrolysis. *NL* is connected to *K* by a U-shaped tube, carrying an outlet tube at the bottom, closed by an indiarubber tube and clip. Since it is

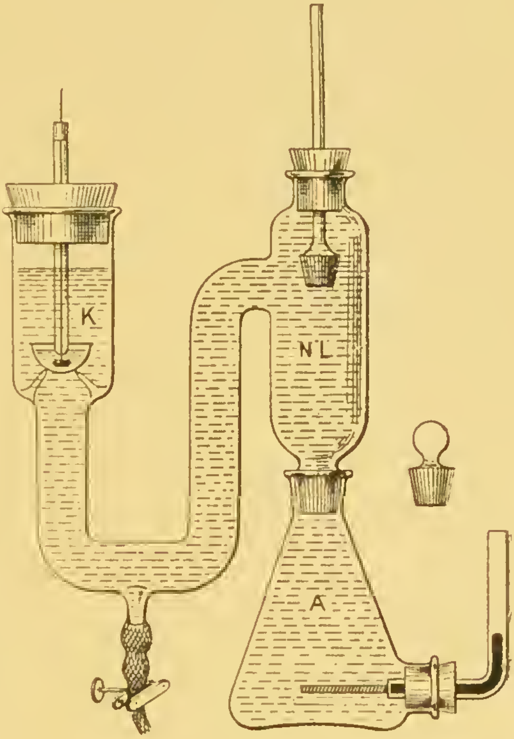


FIG. 43.

only necessary to know the alteration of concentration at *one* electrode, in order to calculate the transport number, the cathode is formed of a small glass vessel, containing mercury and a concentrated solution of zinc or cadmium nitrate. By this means the separation of metal, or the fall of solid impurities, is prevented.

Experiment with a $\frac{1}{20}$ *n* solution of silver nitrate. A rod of silver, such as is used in a silver voltameter, is used as anode. The dried anode chamber is weighed with its stopper and the electrode tube plus mercury, accurate to a centigram, and then filled with solution up to the ground neck, so that all air bubbles are displaced. The upper part is affixed, with its stopper slightly greased, and the whole filled with solution to the wide part of the cathode chamber. Then the small glass vessel, completely filled with mercury and a concentrated solution of zinc nitrate, is placed in position, and in order to keep the layers of the two solutions separate, the zinc nitrate solution is covered with a thin cork layer, through which is thrust a match as handle, and the silver nitrate solution is allowed to fall on the cork from a pipette. A glass tube is thrust through the stopper, and dips below the mercury surface. A copper wire passes through the tube, and acts as connection with the source of current. The opening of *NL* is closed by means of a cork stopper, through which passes the glass rod handle of the inner stopper already referred to. The bent glass tube containing the anode is joined to a piece of rubber tubing, through which a copper wire dips beneath the mercury surface. The whole apparatus is placed in a large water bath in order to conduct away the heat developed by the current. Twenty accumulators, the transport apparatus, and a silver voltameter are arranged in circuit (if such a number of accumulators is not available, the current can be taken from the mains, with the insertion of a suitable resistance). Electrolysis is allowed to proceed until from 0·3 to 0·4 gram of silver has been deposited. It is necessary to make certain that the connections are good, and arranged in the right order.

While the current is passing the materials are prepared for titration by Volhard's method (with thiocyanate, using iron alum as indicator, in nitric acid solution); if not already known the titre of the $\frac{1}{20}n$ thiocyanate solution is accurately measured by an exact titration with a silver salt prepared from electrolytic silver, and the original solution is twice analysed. At the end of the experiment the current is interrupted, the internal stopper cautiously pushed in by means of its handle, and the apparatus taken out of the water bath. After drying, the anode vessel is detached. A few cubic centimetres are pipetted carefully from the anode vessel, the point of the pipette remaining just beneath the surface of the liquid; by this precaution the concentrated layer of liquid at the bottom can afterwards be mixed thoroughly with the rest of the solution. The vessel is then stoppered, and is weighed after the copper wire connection and rubber tube have been removed. The clip is opened and the cathode liquid allowed to flow into the flask containing silver residues; the *NL* solution is collected in a dried weighed glass vessel by raising the inside stopper. The silver voltameter is treated as has already been described, and weighed to a tenth of a milligram. The anode vessel is shaken until the solution is mixed completely; any silver superoxide formed is allowed to settle and the liquid is transferred to a dry weighing vessel. Both the neutral solution and that from the anode chamber are analysed accurately twice (*i.e.*, in two portions). The former must have the same composition as the original solution.

Calculation.—The weight of the deposit in the silver voltameter is subtracted from the weight of the anode vessel. The amounts of silver and of water respectively, contained in the solution, are calculated, and in addition the amount of silver contained in an equal quantity of water before electrolysis (from the analysis of the original solution). From the silver in the anode vessel that set free in the voltameter must be subtracted. It follows that the silver-content is smaller after electrolysis than before. The difference is the amount which has "migrated"; if it is divided by the amount separated in the voltameter, the transport number of silver in silver nitrate is obtained (about 0·47). It scarcely depends on concentration as long as $v > 10$, and rises with rise of temperature (18° 0·471, 30° 0·482). It appears that all transport numbers tend to reach the limiting value 0·5 as temperature rises. The ionic velocities thus become more and more equal. Since conductivity rises with temperature the velocity of the slower ions increases more quickly than does that of the more rapid, so that the less mobile have a greater temperature coefficient.

Applications.—It is well known that the transport number is a sure means of establishing the presence of complex ions. For example, the transport number of copper in a solution of $K_2Cu_2(CN)_4$ would be negative, since it remains in the complex anion, and does not migrate to the cathode; this can be thoroughly established by means of the chemical properties of the solution and its colour, as well as by cryoscopic measurements.

By a combination of the value of Λ_∞ with the transport number the **mobility** of **single ions** is obtained (see Table V.). Thus if $\Lambda_\infty = u + v = 116$ for silver nitrate at 18°, then

$$u_{Ag^{\cdot}} = \frac{u}{u+v}(u+v) = 0{\cdot}471 \times 116 = 55, \text{ and } v_{NO_3'} \doteq 61;$$

at 25° $\Lambda_\infty = 134$, the transport number is 0·478, and the consequent mobility of $Ag^{\cdot}$ 67, that of NO_3' 70.

Hence the temperature coefficient of the conductivity is about 2·2 per cent., that of $u_{Ag^{\cdot}}$ about 2·3 per cent., and that of $v_{NO_3'}$ about 2·1 per cent.

Since the values of Λ_∞ are all obtained by extrapolation, they are always somewhat more uncertain than those of Λ. It would appear that formerly the values for some mobilities were supposed too high, especially that for hydrogen.

If the mobility is known, Λ_∞ can be calculated for substances so weakly dissociated that with the most dilute solutions which can be used (v=2000—5000), the observed values are still very far from the limiting value. Examples are certain organic acids, or substances, such as AgCl, $BaSO_4$, etc., in which κ can be measured accurately, but the concentration cannot be estimated directly (see p. 140).

A further application of transport numbers is found in the calculation of the electromotive forces of concentration cells (see p. 158).

In the case of coloured ions the *absolute* migration velocity (cm. per second for a potential fall of 1 volt per cm.) can be easily measured; *e.g.*, for MnO_4' by observations in a

U-tube containing dilute $KMnO_4$ solution, and above it a layer of KNO_3 solution of equal normality. The platinum electrodes dip into the colourless solution.

If the absolute migration velocity is multiplied by 96540, the mobilities are obtained, denoted above by u and v; $v_{MnO_4'}$ is about 52 at 18°.

CHAPTER XI

MEASUREMENT OF DIFFERENCES OF POTENTIAL

Preparation of Normal Elements.

A description has already been given (p. 111) of the methods in which a cadmium normal element (a **Weston cell**) and a zinc element (a **Clark cell**) are put together. The former has the smaller but more constant potential. It is prepared with a solution of $CdSO_4, \frac{8}{3}H_2O$ saturated at 4°, or in practice with solution plus excess of solid.

The cell is built up in an H-shaped vessel, 1—1·5 cm. wide; a platinum wire is fused through the bottom of each limb. One wire is covered with *pure* mercury; into the other chamber is poured, by means of a funnel, a warm 10—12 per cent. of cadmium amalgam, also prepared from *pure* material. On cooling the amalgam solidifies in the vessel; the walls must not be soiled with splashes of metal. Over the mercury a second layer is added through a second clean filter, also without touching the walls; it consists of a well-mixed paste of

$$Hg, HgSO_4, CdSO_4 + \frac{8}{3}H_2O,$$

and a few drops of saturated solution of $CdSO_4$. Both limbs are packed with small crystals of cadmium sulphate to a height of 1 cm. and the whole vessel filled with saturated solution to within about 1·5 cm. from the lip. As a safeguard the vessel can be filled up with larger cadmium sulphate crystals. At the top of both limbs a thin layer of liquid paraffin is added, the vessel is closed with good corks cut off level with the glass rims and well sealed. A small air cushion is left underneath each cork. The vessel is placed astride a suitably cut large cork, which is sealed with wax to a small wooden stand. The platinum wires should not come in contact with the stand. It should have been soaked in paraffin previously for good insulation (by heating it in melted paraffin for some minutes at 100°). The student should convince himself that fresh wood (on account of the salts contained in the sap) conducts current perceptibly, but, when paraffined, conducts no longer. In the end of the stand two binding screws are fixed, and to the bodies of these are soldered thin spirals of copper wire in such a manner that the bores remain free and the screws movable. The ends of the wires are twisted to very thin spirals looped over the bent platinum wires and cautiously soldered to them. There must be no tension on the wires. The binding screw connected with the mercury pole is marked with a +, the other with —; thus a complete normal element is obtained, which, with cleanly work and use of pure materials, is accurate to within a ten-thousandth of a volt, and consequently to some hundredths per cent. Especial care must be taken that it is used free, or almost free from current (0·00005—0·0001 ampere); it contains a quite considerable resistance, which can easily amount to 2000 Ω. This is not remarkable considering the way in which it is built up.

A **Clark cell** is prepared in a similar manner. The zinc must be free from cadmium and arsenic. The saturated solution of zinc sulphate is boiled with excess of solid and a small quantity of zinc dust, and, after cooling, filtered. The solubility of zinc sulphate has a much greater temperature coefficient than that of cadmium sulphate, and in consequence the electromotive force changes to a much greater extent. A considerable excess of crystals must be added, and large variations of temperature avoided, since equilibrium between solid and solution, and with it a constant electromotive force, are established very slowly in a solution at rest. Every measurement with a Clark cell requires a temperature observation.

Comparison of Electromotive Forces by Fechner's Method.

If a very large resistance is included in a circuit, the deflection of the galvanometer for two different sources of currents will be proportional to the respective electromotive forces of these elements (Fechner's Method). In this way a Clark and a Weston cell can be compared with one another. Since, however, the internal resistances of these cells may differ by about 1000 Ω, several 100000 Ω must be inserted, which is inconvenient. To obviate this, the cells are measured together, first arranged in the same direction (deflection b), then in opposite directions (deflection a); in this way the resistance $(R + r_i + r_i')$ is always the same, and the deflections a and b are proportional to Cl + We and Cl — We. The E.M.F.'s of the two elements are therefore in the ratio $\frac{a+b}{a-b}$. A sensitive mirror galvanometer in circuit with a commutator is used in this experiment, and, for the large resistance, a 100000 Ω box. If the galvanometer is too sensitive, a resistance box is placed in series with it, and plugs removed until suitable deflections are obtained with the two arrangements. The current is reversed, and the mean taken. Experiments should be made once, with the Clark alone (deflection c), then with the Weston alone (deflection d); the ratio will not quite equal $\frac{a+b}{a-b}$. An attempt should be made also to calculate the internal resistances of the two elements, from the arrangements Cl + We, Cl alone, We alone. Three measurements are necessary, since the sensitiveness of the instrument (α) also enters into the equation.

$$\left[\frac{\text{We} + \text{Cl}}{100000 + r_i + r_i'} = \alpha\, a\,;\ \frac{\text{We}}{100000 + r_i} = \alpha\, c\right.$$

$$\left.\frac{\text{Cl}}{100000 + r_i'} = \alpha\, d\right].$$

Since c is only slightly greater than $\frac{a-b}{2}$, and d only slightly greater than $\frac{a+b}{2}$, the measurements must be very accurate, in order to calculate r_i and r_i' by this method. The values are found more accurately if the large resistance is varied, and measurements made with the arrangements, Cl + 100000 Ω, Cl + 70000 Ω, We + 100000 Ω, We + 70000 Ω. In any case it can be shown in this way that $\frac{a+b}{a-b}$ is the correct value. The interpolation formula for different temperatures is given on p. 111.

Measurement of the Electromotive Force of an Accumulator. Testing of Voltmeter.

By the same method are measured Acc — We, Acc + We, Acc + Cl, Acc — Cl, and the E.M.F. of the accumulator calculated. The accumulator is then connected with a voltmeter (an accumulator tester). If a different E.M.F. is found than by Fechner's method the difference is the "correction" of the voltmeter for the value concerned (2 *V*). With the very slight internal resistance of the accumulator the error with a direct comparison of accumulator and normal element would be very great.

Compensation Method of Poggendorff—du Bois-Reymond.

The compensation method is more elegant than that of Fechner. The electromotive force *e* which is to be measured is so arranged with respect to a second that the quantities measured are made equal and the galvanometer is not deflected. The galvanometer *G* is used here as an Amperemeter, and really as a null instrument. As comparison E.M.F. a battery is taken (the element of work *E*) whose E.M.F. is greater than that which is to be measured. It is decreased by connecting it with a large variable resistance (see p. 111).

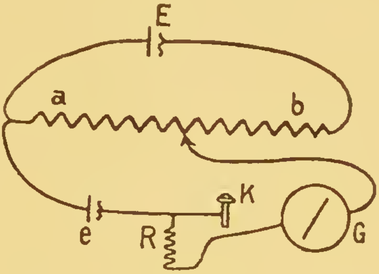
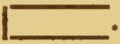


Fig. 44.

The arrangement is shown in the diagram (see Fig. 44). As element of work *E*, *one* accumulator can always be used. Its E.M.F. is measured before or after the experiment by comparison with a normal element. *K* is a key, with which the ballast resistance *R* which protects the galvanometer *G* can be cut out, if the galvanometer deflections are too small. *E* is joined to $a + b$ by thick wires whose resistance is small compared to $a + b$; if the galvanometer is not deflected when it is connected to the length *a*, then

$$e = E \frac{a}{a + b}.$$

E can be joined to a cylinder bridge such as is used for conducting measurements and the bridge divided by means of the small sliding wheel. However, it is most suitable to employ a large resistance. It is apparent that the resistance of the galvanometer current circuit (r_i from e, ballast resistance, galvanometer resistance) is completely negligible, since a null method is employed. The magnitude of the resistance employed depends entirely on the sensitiveness of e and G. If an accurate adjustment to zero cannot be made, two deflections must be determined, on opposite sides of the zero point, and the zero value found by interpolation from these and the corresponding resistances; the method is exactly like that for an accurate weighing.

If a resistance box is employed, the calculation can be simplified by taking a round number for $a + b$. The following arrangement is convenient: Two quite similar resistance boxes, each of 10000 Ω, are selected, which are arranged in the manner . To the ends of one are connected e, K, R, and G, whilst E is joined to both boxes. The whole of the plugs of the box to which e is joined are drawn out, so that the current circuit has a resistance of 10000 Ω.

Then the resistance in the small current circuit is diminished and with it the opposing potential, until the null instrument comes to rest; the plugs extracted are always transferred to the corresponding places in the other box, so that the total resistance always remains at 10000 Ω, and

$$e = E\frac{a}{10000}.$$

The elegant **compensation apparatus of Wilsmore** (Edelmann, Munich) is used in the same way. Two similar resistance series, each of from 100 Ω to 0·05 Ω, are each contained in boxes facing one another, and joined to one another at one end. Only one series is provided with plugs. The sum of each series is 200 Ω.

If a potential difference of exactly 2 volts is joined to the free ends of the two connected series (see below) every Ω of the fall corresponds to 0·01 volt, and consequently the 0·05 Ω piece to a half millivolt. Accordingly, if the plugs are removed and pushed into the corresponding holes, the potential fall can be obtained in either the one or the other resistance series. Hence by comparison with measured potential differences it is possible to measure any E.M.F. between 2·000 and 0·0005 volts. While the plug holes of the upper series are marked with the number of ohms, on those of the lower are marked the corresponding volts. In other respects the arrangement is similar to those already described (Galvanometer, Ballast resistance and key).

The fall of potential of exactly 2 volts is obtained in the following way. A circuit is made up of an accumulator (E.M.F. $> 2\ V$), a resistance with sliding contact, which at most consists of 20 Ω, and the measuring apparatus. To the binding screws of the apparatus is joined an accumulator tester, and the resistance is regulated so that the instrument registers 2·00 volts (a rough reading). In the second series of resistances are inserted $101{\cdot}85\ \Omega = 1{\cdot}0185\ V$, which is the E.M.F. of a Weston cell; the second circuit is made up with the Weston (opposed to the accumulator), this resistance series, a null instrument, along with its protecting resistance and key. If the accumulator gives exactly 2 volts, the null instrument will remain at rest. If this is not the case, the resistance is adjusted, or, preferably, a larger resistance is inserted in parallel (see p. 117) until the instrument is no longer deflected. It must be observed particularly that since the normal cell must only be used in a circuit practically free from current, the balancing E.M.F. must be inserted *before* the normal cell.

Since an accumulator, when not quite freshly charged, maintains the same potential for a long time, the apparatus, when once in working order, can be used for a large series of measurements, since in such measurements but very little current is used up.

In this way an accumulator tester can be standardised by the help of a Weston; this cannot be carried out by direct comparison, since the Weston would be ruined, while the greater part of the E.M.F. would be used up in overcoming the internal resistance, so that the voltmeter would show a *far too small* potential.

Concentration Cells.

Two completely dissociated solutions of a univalent binary electrolyte, whose concentrations are c_1 and c_2, are in contact with one another. In order to equalise the differences of concentration it is necessary (cp. p. 40) to accomplish the osmotic work $RT \ln \frac{c_1}{c_2}$ for every gram-ion, since $\frac{c_1}{c_2}$ is equal to the ratio of the osmotic pressures. If it is wished to make the equalisation electrically, 96540 coulombs must be passed through the boundary surface of the solutions per gram-equivalent in order to dilute the concentrated solution. Thereby $\frac{u}{u+v}$ cations will migrate with the current, $\frac{v}{u+v}$ anions in the opposite direction. The work to be accomplished electrically is therefore

$$RT \frac{u}{u+v} \ln \frac{c_1}{c_2} + RT \frac{v}{u+v} \ln \frac{c_2}{c_1} = RT \frac{u-v}{u+v} \ln \frac{c_1}{c_2},$$

where R is now expressed in electrical units (electrolytic gas constant, $= 0{\cdot}861 \times 10^{-4}$; see p. 112). In this way a potential difference is obtained at the surface of separation. If $\frac{1}{10}$ and $\frac{1}{100}n$ solutions of $AgNO_3$ are used at 18°, then $\frac{u-v}{u+v}$, the difference of the transport numbers of Ag and NO_3 is equal to $0{\cdot}471 - 0{\cdot}529 = -0{\cdot}058$, and the potential difference at their boundary layer, if both solutions are assumed to be completely dissociated,

$$= -0{\cdot}058\ (0{\cdot}861 \times 10^{-4} \times 291 \times 2{\cdot}303) \text{ volt}$$
$$= -0{\cdot}058 \times 0{\cdot}0577 \text{ volt} = -0{\cdot}0033 \text{ volt}.$$

With KCl solutions the potential difference will be almost nil, since the transport numbers are almost equal; with HCl solutions, with the large cathode transport number 0·83, the potential difference will be + 0·032 volt.

According to Nernst every metal has a definite tendency to give ions to the solution, which is the greater, the less noble the metal. If the solution, through this tendency, the *solution tension*, had a definite ionic concentration C, no potential difference would exist any longer between metal and solution.

If the concentration of the solution is c, the difference of potential, if the metal gives univalent ions, is $RT \ln \frac{C}{c}$; if they are N-valent, it is $\frac{RT}{N} \ln \frac{C}{c}$. The deduction is similar. If there are two solutions of a binary electrolyte of different concentrations between two electrodes of the corresponding metal, *e.g.*, Ag, $AgNO_3$ solution of ionic concentration c_1, $AgNO_3$ solution of ionic concentration c_2, Ag, then there are three potential transitions in the system:—

1. Ag/solution c_1: $RT \ln \frac{C}{c_1}$.
2. Solution c_1/solution c_2: $\frac{u - v}{u + v} RT \ln \frac{c_1}{c_2}$.
3. Ag/solution c_2: $RT \ln \frac{C}{c_2}$.*

Hence the difference of potential between the two silver electrodes is

$$\pi = RT \ln \frac{C}{c_1} + \frac{u - v}{u + v} RT \ln \frac{c_1}{c_2} - RT \ln \frac{C}{c_2}$$

$$= -\frac{2v}{u + v} RT \ln \frac{c_1}{c_2}.$$

At 18°, if the ionic concentrations are in the ratio 10 : 1, then

$$\pi = -\frac{2v}{u + v} \cdot 0{\cdot}0577 \text{ volts.}$$

The same results are obtained if the solutions are $1n$ and $0{\cdot}1n$ with respect to the ions, or $0{\cdot}01n$ and $0{\cdot}001n$. If an indifferent salt is employed to connect the solutions, so that the silver ion scarcely takes part in the current flow, the potential difference falls off between the two solutions, and, neglecting sign, there results

$$\pi = RT \ln \frac{c_1}{c_2} \text{ or } = 0{\cdot}058 \log_{10} \frac{c_1}{c_2},$$

where c_1 and c_2 can be taken equal to the normalities, if dilute solutions are used.

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* The E.M.F. of a cell with different electrodes, *e.g.*, a Daniell's cell, can be summed up in the same way.

The current flow in a cell always takes place from the dilute to the concentrated solution. If the cation has the valency N, in general

$$\pi = -\frac{2v}{u+v} \cdot \frac{RT}{N} \cdot \ln \frac{c_1}{c_2}.$$

It is obvious that the determination of π can be used to find the ionic concentration of a solution, if that of the solution used for comparison is known. If it is found, *e.g.*, that π is equal to 0·450 volt, when c_1 is $\frac{1}{100}$, then

$$c_2 = c_1 \times 10^{-\frac{0·450}{0·058}} = 10^{-2} . 10^{-7·76} = 10^{-9·76},$$

since π is equal to 0·058 volt for each power of ten in the difference of concentration.

The above results can be found directly (less exactly) if the solution c_2 is brought osmotically to the concentration c_1, and the work calculated in electrical units ($R = 0·861 \times 10^{-4}$).

Exercises.

1. Measure the cell Ag / 0·1n $AgNO_3$, 0·01n $AgNO_3$ / Ag. Prepare the electrodes from thin strips of pure silver, to which bind wires. Test first whether a difference of potential exists when both electrodes dip into the same solution. If there is a difference greater than 0·0005 volt, the electrodes must be joined and immersed in a $AgNO_3$ solution for twenty-four hours before the experiment is performed.

Place the solutions in small H-shaped vessels, and fix these into corks, or by sealing-wax to small wooden stands. Into the two empty vertical limbs bring the ends of a ┌┴┐ shaped syphon, and carefully suck up the solutions by a rubber tube into the syphon till they join. Then close the tube by a pinch-cock.

Make the measurement with a cylinder bridge, with either two resistance boxes, or the compensation apparatus; make a second reading with $n KNO_3$ solution in the syphon.

2. Measure the cell Ag / 0·01n $AgNO_3$ solution, 0·001n $AgNO_3$ solution, / Ag, with KNO_3 solution in the syphon.

3. Replace the 0·001n $AgNO_3$ solution by KNO_3 solution

+ AgCl, and calculate the concentration of the AgCl. It should be, as in pure water, 1×10^{-5}.*

In such a dilute solution the solute can be considered as practically completely dissociated. The product of the two ionic concentrations is therefore

$$[\mathrm{Ag}^{\cdot}]\ [\mathrm{Cl}'] = [\mathrm{Ag}^{\cdot}]^2 = 10^{-10}.$$

4. Pour into one H-vessel $0{\cdot}1n$KCl solution + AgCl, into the other $0{\cdot}01n$ $AgNO_3$, and join them by means of KNO_3 solution. Calculate the concentration of the $Ag^{\cdot}$ ions from the E.M.F., and show thus that the product

$$[\mathrm{Ag}^{\cdot}]\ [\mathrm{Cl}'] = 10^{-10}.$$

The concentration of the Cl' ions can be taken as 0·1 without introducing a great error. (Validity of the law of mass action; constancy of ion products; influence on solubility.)

5. Dissolve the AgCl in concentrated ammonia solution, and again use the KNO_3 syphon. If no Ag-ions existed in the complex silver ammonia solution, an infinitely great difference of potential would be found. Actually it is only 0·4—0·5 volts. Calculate from this the concentration of Ag-ions. The E.M.F. method of analysis thus also permits quantitative measurements in solutions, where most chemical reactions fail.

Electrode Potentials.

In order to measure a single potential, the pair, metal and solution, which form it, are combined with a **normal electrode**, and the potential of the cell measured, from which is subtracted the corresponding value for the normal electrode.

As normal electrode can be used:

1. the combination: mercury, calomel, and a nKCl solution saturated with calomel (*calomel electrode*).

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* The same number is obtained from the specific conductivity of a saturated solution of AgCl (after the conductivity of water has been subtracted). Kohlrausch found that at 18°

$$= 1{\cdot}24 \times 10^{-6}.$$

Since the mobility of Ag = 55, and that of Cl = 65 (p. 150), the ionic concentration of Ag is $\frac{\kappa}{\Lambda_\infty} = \frac{1{\cdot}24}{120} \times 10^{-6} = 1 \times 10^{-8}$ per cubic centimetre, and therefore 1×10^{-5} per litre. At 34° the concentration is already $2{\cdot}1 \times 10^{-5}$ (cf. p. 59).

2. platinised platinum immersed in normal sulphuric acid and saturated with hydrogen (*hydrogen electrode*).

In order to prevent precipitation and differences of potential arising from the solutions diffusing into one another, the normal electrode and the second electrode with its solution are joined by a syphon filled with KNO_3 solution. The potential arising from diffusion between, on the one hand, nKCl solution and salt solutions, and, on the other, acids and nH_2SO_4, is slight, so that no solution need be placed between.

Most work is done with the calomel electrode, which is put together once and for all, while chemists are agreed to refer the potentials measured to that of the hydrogen electrode. The hydrogen electrode compared with the calomel electrode gives a potential of + 0·283 volt, which is almost independent of temperature.

The Calomel Electrode.

A test tube is taken with side tube blown on. Mercury is poured into it, and is covered with a paste of Hg, pure powdered calomel, and nKCl solution, which paste has often been shaken up with KCl solution. Over it is poured a KCl solution saturated previously with calomel, and the tube filled so full that the solution partly fills the side tube. The glass tube is closed by a cork stopper with leading tube closed by a rubber tube and screw clip. Through a second hole in the cork passes a glass tube, into the lower end of which is sealed a platinum wire. The external part of the wire is immersed completely in the mercury. The tube is filled with mercury, into which dips the connecting wire. The side tube dips into a small glass beaker containing $2n$ KNO_3 solution, which can be connected by means of a syphon with the second electrode. (Or the second electrode can be built up in a similar form with side tube, which also dips into the glass beaker.) The tube in the cork serves to renew the solution in the side tube.

Exercise. — Measure the potentials Zn / $nZnSO_4$ and Cu / $nCuSO_4$. By subtraction (whereby it is unnecessary to reduce the potentials measured to that of the hydrogen electrode), the E.M.F. of the *Daniell cell* is obtained. Calculate the ionic concentration of Cu and Zn corresponding to the solution pressures according to the formula $\frac{RT}{N} \ln \frac{C}{c}$, where N is equal to the valency of the ion, and therefore in this case $= 2$.

Use in the first place Poggendorff's compensation method with a needle galvanometer (as shown in Fig. 44). The arrangement

normal electrode, KNO_3, $n ZnSO_4$ / Zn

is joined as described. (The solutions of KNO_3 and $ZnSO_4$ can be connected roughly by moist filter paper dipping into both.) This forms the cell e of the circuit (*cp.* the figure). When the position of the sliding contact has been found, for which the galvanometer is not deflected, the Zn and $ZnSO_4$ are replaced by Cu and $CuSO_4$, and the voltage again measured.

The Zn and Cu electrodes are formed simply by taking plates of Zn or Cu, to which are soldered connecting wires and immersing them almost completely in the respective solutions contained in glass beakers.

When the measurements have been completed, replace the galvanometer by a capillary electrometer (see p. 125), and repeat the measurements.

Decomposition Potential.

In order to set free the ions at an electrode, a characteristic potential is necessary for every ion, which is given by the expression $\frac{RT}{N} \ln \frac{C}{c}$. If the potential used remains less than the sum of the potentials necessary for the two ions, no electrolysis takes place. The quantity just sufficient is named the *decomposition potential*, and, as is seen from the expression given, it depends on the concentration of the ions in such a way that, with univalent ions, for each diminution of concentration by a power of ten, it increases by 0·058 volts. The decomposition tension of the cation or the anion can be measured by means of a third, a normal electrode introduced into the solution near the anode or cathode; it is more convenient to measure that E.M.F. at which the current strength abruptly attains a considerable value; at that E.M.F. the opposing force is overcome. The tension in the solution is increased gradually, and tension and current intensity are measured at the same time.

The values are plotted on squared paper, and in most cases a sharp break in the curve is obtained, which corresponds to the decomposition tension, unless there is considerable resistance in the circuit, which likewise uses up potential. From the observed value *V*, the value *ir* must be subtracted in order to obtain the potential consumed only in electrolysis.

In this case, again, the potential of hydrogen is referred to as zero value. In working with acids, a large piece of platinised platinum foil, saturated with hydrogen, is used as cathode, and a short platinised platinum wire as anode.

Exercise.—Decomposition potential of the three hydrogen halides in normal solution (Fig. 45).

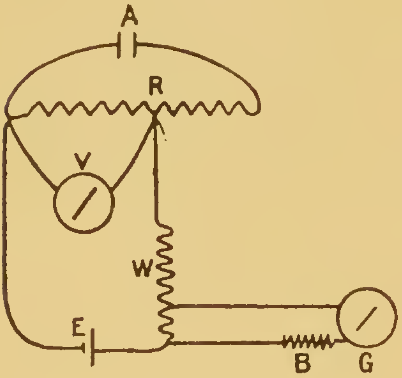

Fig. 45.

An accumulator is closed with a Ruhstrat resistance *R*, which carries three binding screw connections; the movable connection is joined to an accumulator tester *V*, and through a resistance box *W* to one electrode of the cell which contains the acid whose decomposition potential is to be measured. The end of the rheostat is joined with the other connection of the voltmeter and the second electrode. A second circuit is taken off from a small resistance in the box to a delicate mirror galvanometer *G*, to which is connected a ballast resistance *B*. The platinum strip is the cathode, and is not quite immersed in a *n*HCl solution; a constant stream of small bubbles of hydrogen rise around it.

V and *G* are read after every alteration of the resistance *R*; at first it is decreased in large steps, until a considerable deflection is obtained, when immediately the resistance is decreased below the critical value and *V* increased by small steps.

As soon as the galvanometer begins to be unsteady the tension is not further augmented, but the next solution measured. This consists of a solution of HCl, to which some KBr has been added, thus yielding a solution of HBr; in the same way KI is dissolved in HCl. When the break in the curve is not sharp the almost horizontal and the almost vertical branches are produced until they cut.

In order to find the current strength which corresponds to the deflection of the galvanometer at the decomposition point, and thereafter if necessary to correct for ir, the galvanometer is calibrated. In previous measurements the current strength only came into consideration relatively, but here we require to know the number of amperes accurately. Instead of the decomposition cell, the accumulator, and the rheostat, a normal element is inserted with from 10000 to 100000 Ω, the deflection measured, and the sensitiveness of the galvanometer calculated for the former arrangement. If $ir > 0{\cdot}001$ volt, it must be subtracted from V.

For multivalent electrolytes a particular decomposition tension corresponds to every kind of ion. A knowledge of the decomposition tensions is important for electrolytic separations.

Thermo-couples.

If the ends of two wires of different materials (metals or alloys) are soldered together to form a ring, and if the two junctions are kept at different temperatures, an E.M.F. will be produced. Its value depends on the kind of material used; it will be always proportional to the difference of temperature. If one metal is antimony, the other bismuth, a temperature difference of one degree will correspond to 0·100 millivolt; the corresponding value for iron-constantan is 0·053, and for copper-constantan 0·040 millivolts (see p. 120). With an arrangement consisting of a platinum wire and an alloy of 90 per cent. platinum and 10 per cent. iridium or rhodium, one degree difference at high temperatures corresponds to 0·010 millivolt.

For temperature measurements thermo-couples possess many advantages over mercury thermometers. They are much smaller and occupy so little space that they can be placed easily in small apparatus; they do not lag but attain the correct temperature very rapidly. They can be used at the extremes of temperature, at which mercury is inapplicable. To increase their accuracy, a number can be combined in series, when their E.M.F.s are added. Such electrical quantities, at least in principle, can be measured very accurately. Thermo-couples are used especially to measure very high or very low temperatures, or to determine with exactitude differences of temperature (as in cryoscopic or ebullioscopic measurements, or where change of temperature must be followed very exactly.

For low temperatures (+ 4000 to the temperature of liquid air) either of the combinations Fe-constantan, or Cu-eureka can be used advantageously. For temperatures between 400° and 1600° the platinum-platinum-rhodium combination can be used.

To make a Fe-constantan or Cu-eureka couple, an end of each is soldered together, and the other ends not soldered together, but each to a thick copper or brass wire, and these are connected to the binding screws of a galvanometer and a resistance box respectively. The soldered point of the thermo-couple is kept at the temperature which is to be measured, the other ends, those joined to the brass wires, are kept apart and well insulated from each other, at a known constant temperature (either zero, in a water-ice mixture, or at room temperature measured with a mercury thermometer. In the latter case, which is convenient for most rough measurements, the brass wire connections should be immersed in a petroleum bath, which is a sufficiently good insulator, or both wrapped in cotton wool, and placed with a thermometer, in a beaker filled with cotton wool, which is kept at some distance from any source of heat).

Thermo-couples must be calibrated from time to time by measuring the E.M.F.s which correspond to fixed temperatures (as 0°, 100° the boiling point of water, the boiling point of sulphur (see below), 1064° the melting point of gold, or −78·2° the eutectic temperature of a mixture of solid CO_2 and ether. The fixed points selected must lie just within the range of temperature over which the thermo-couple is to be employed. The resistance of the wires increases with temperature, and to get rid of this effect a large resistance should be included in the circuit (before calibration). It is very convenient to measure the E.M.F. by a millivoltmeter of good make instead of a galvanometer. It is calibrated previously by comparison with a normal element or by means of Poggendorff's compensation apparatus (see p. 155). Some firms make special millivoltmeters (*pyrometers*) for measurement of temperature, which contain next to the millivolt scale another which gives roughly the corresponding temperature obtained with a platinum-platinum-rhodium element. It is of course useless for any other couple. These instruments have usually a great resistance, so that the resistance variations in the thermo-couple can be neglected, and no special resistance need be placed in the circuit.

The range of a thermo-couple (or of the millivoltmeter) can be increased by the insertion of resistances.

Since iron, constantan, copper, and eureka are all rather easily attacked by vapours (water, sulphur, etc.), the junction of the wires and solder should be enclosed in a small glass capillary, in order to protect them during a calibration. If possible, the wires should be insulated with a silk cover.

Exercise.—Measure the E.M.F.s corresponding to the following temperature differences:

$0°$ — room temperature; room temperature — $100°$, room temperature — boiling point of sulphur ($444{\cdot}6° + \frac{b - 760}{12}$; b = barometric pressure). Try to plot the connection between temperature and E.M.F., and calculate the quadratic equation to which the curve corresponds.

Oxidation and Reduction Cells and Mechanism of Current Production.

If a hydrogen electrode (platinised platinum immersed in nHCl, and saturated with hydrogen) and a chlorine electrode, formed in an analogous manner, are combined together, the resulting **Chlorine Knallgas element** gives an E.M.F. of about

1·36 volts at room temperature, if the gases are under atmospheric pressure.

Exercise.—A three-necked Wolff's bottle, of which the middle neck is narrower than the others, is taken and filled with the acid. A test tube, also completely filled with acid, is fixed through each of the outer necks; it contains a platinum wire fused through the upper end, to which is soldered a long strip of platinum foil (see Fig. 46). The platinum foil extends nearly the whole length of the tube.

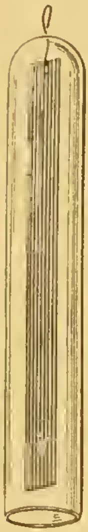

Fig. 46.

Through the middle neck is passed a platinum wire as anode, and the solution electrolysed until the foil in one tube is two-thirds exposed to electrolytic hydrogen. (In this tube the foil is platinised.) The other tube, which contains ordinary foil, is two-thirds filled with chlorine.

The cell so formed is tested by means of pole-reagent paper (see p. 114) to ascertain which pole is anode and which is cathode, and the E.M.F. is then measured. If the cell is joined to an amperemeter, a perceptible current is obtained, whilst equal volumes of hydrogen and chlorine disappear, producing hydrochloric acid, *i.e.*, gaseous, electrically neutral elements become ions by taking up positive or negative charges respectively:

$H_2 + \oplus \oplus = 2H^{\cdot} - \oplus$; $Cl_2 + \ominus \ominus = 2\,Cl' - \ominus$.

This action can be compared with the chemical action in a Daniell's cell, with the following result: in the chlorine knallgas cell ions are formed at both poles, but in the Daniell only at one, at the zinc ($Zn^{\cdot\cdot}$); on the other hand, an equivalent cation ($Cu^{\cdot\cdot}$) disappears at the copper electrode. Discuss in the same way the actions which take place in the concentration cells previously described (p. 160). In all these cases the production of an anion is associated with the disappearance of a cation, or *vice versâ*. The production of cations ($Zn \longrightarrow Zn^{\cdot\cdot}$, $H_2 \longrightarrow 2H^{\cdot}$) corresponds chemically to oxidation, the production of anions ($Cl_2 \longrightarrow 2Cl'$) to reduction. The two actions always take place side by side at the two electrodes of the cell, and furnish the energy of the current.

If the actions take place with one and the same metal, *no* current is produced, *e.g.*, by the solution of Zn in $H_2\,SO_4$: $Zn + H^{\cdot} + H^{\cdot} + SO_4'' = Zn^{\cdot\cdot}\,SO_4'' + H_2$. If, on the other hand, the zinc is joined to a platinum wire through an amperemeter, when the two metals are immersed in sulphuric acid a current is observed, since now the production of $Zn^{\cdot\cdot}$ ions and the disappearance of $H^{\cdot}$ ions take place from the different metals. Bubbles of hydrogen are set free at the platinum only, while at the zinc sinks a somewhat heavier layer of concentrated zinc sulphate solution. (This can be tested by experiment.) Every galvanic element can, in accordance with this view, be considered as an oxidation and reduction cell. However, the expression is usually confined to cells which contain the typical oxidation or reduction material. Such substances react with changes of valency, and therewith, of charge (*e.g.*, $Mn^{VII}O_4' \longrightarrow Mn^{II\cdot\cdot}$, $Cr^{VI}O_4'' \longrightarrow Cr^{III\cdot\cdot\cdot}$, $Sn^{II\cdot\cdot} \longrightarrow Sn^{IV\cdot\cdot\cdot\cdot}$, etc.).

To the oxidation and reduction cells in the narrow sense belong the types frequently used as sources of current: Bunsen cell, Leclanché cell, and the Bunsen type of immersion battery (bichromate cell). In these three cells the respective reduced or oxidised substance is zinc, while in all three, the other electrode consists of charcoal. The E.M.F.'s of the three, however, differ considerably, since the oxidising agents, MnO_2, HNO_3, CrO_3, possess a considerably differing oxidising capacity (oxidation potential).

Exercise.—Measure the difference of potential between zinc and charcoal in dilute sulphuric acid; here no reduction takes place in the restricted sense of the word. Further measure the E.M.F. of the three cells above-mentioned. Make all the measurements by laying the poles of the cell directly on the voltmeter connections, and reading to 0·01 volt. Convince yourself of the inconstancy which results with stronger currents (short circuit) or longer passage of current, for which purpose take amalgamated zinc, *dilute* sulphuric acid, *dilute* potassium bichromate solution, and gas or arc lamp carbons. The exhaustion is due to the diminishing oxidation capacity of the chromic acid, and the opposing osmotic pressure of the zinc ions; partial recovery takes place with stirring, since the products of reaction are removed from the electrodes, and replaced by fresh solution.

Make up a fourth cell with zinc, carbon, and a dilute solution of potassium permanganate.* Always measure directly with the voltameter, as above.

The E.M.F. depends on the concentration of all the ions produced or disappearing through the oxidation and reduction actions taking place.

The influence of the concentration of the ions which are disappearing is best studied in a simple case, namely, a single electrode, which is combined with a normal electrode (see above). For this purpose a MnO_2 electrode immersed in H_2SO_4 is well adapted; MnO_2 conducts metallically, like charcoal.

To prepare the electrode, a strong solution of nitric acid and manganous sulphate is electrolysed with 2 volts, and at most 0·1 ampere for a few minutes, the anode consists of well-washed platinum foil, and the cathode of a platinum wire. The precipitate of MnO_2 must be thin but coherent. It is desirable to prepare a second similar electrode in the same manner. After washing with water they must be allowed to stand overnight in very dilute sulphuric acid solution, and connected together by a wire (short circuited).

The reaction which takes place in the element

$$MnO_2 \ / \ H_2SO_4 \ / \ \text{Normal electrode}$$

consists in the reduction of MnO_2 to $MnSO_4$, and the oxidation of $H^{\cdot}$ ions to water; written ionically, this becomes

$$MnO_2 + 4H^{\cdot} + \ominus + \ominus = Mn^{\cdot\cdot} + 2H_2O.$$

In the normal electrode the two remaining positive electric charges are compensated by the two negative charges set free (formula?)

To reduce 1 gram-molecule of MnO_2 consequently 2 equivalent charges, each of 96540 coulombs, will be used up. The reaction is therefore, electro-chemically, bivalent.

In order not to exhaust the normal electrode it is used like normal elements, either free from current, or externally compensated. Therefore a voltmeter is not used, but a compensation method. To connect the MnO_2-electrode with a normal electrode an approximately twice normal solution of KNO_3 is inserted between the two; thus the by no means insignificant liquid potential which results from the very different mobilities of the Cl′ and H· ions is avoided (see p. 158).

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* The electrodes, well insulated, are clamped close together in an ordinary laboratory stand; the solution is placed on an easily movable block.

If two MnO_2 electrodes which are immersed in solutions containing different concentrations of H· and Mn·· (C_H and C_{Mn} in one, C_H' and C_{Mn}' in the other) are opposed to one another, a concentration cell is obtained of which the E.M.F. is

$$\pi = \frac{RT}{2}\left(\ln\frac{C_H^4}{C_{Mn}} - \ln\frac{C_H'^4}{C_{Mn}'}\right) = \frac{RT}{2}\ln\frac{C_H^4\,C_{Mn}'}{C_H'^4\,C_{Mn}}$$

since one Mn·· ion appears for the disappearance of 4 H· ions, and the constant factor RT must be divided by the degree of the reaction (in this case 2).

Hence if the concentration of the Mn·· ions is constant, whilst that of the H· ions is increased ten times,

$$\pi = \frac{RT}{2}\ln 10^4 = \frac{0{\cdot}058}{2}\log_{10} 10^4 = 0{\cdot}116 \text{ volt.}$$

If, on the other hand, the H· concentration is constant, and that of the Mn·· ions is increased tenfold, then

$$\pi = -\frac{RT}{2}\ln 10 = -0{\cdot}029 \text{ volt};$$

i.e., the difference of E.M.F. is only one-fourth as great, and in the opposite direction, since the Mn·· ions exert an *opposing* osmotic pressure. Instead of arranging two MnO_2 electrodes in opposition, it is more convenient to arrange a single E.M.F. alternately with and against a normal electrode, and to take the difference of the two numbers so obtained.

Exercise.—Immerse the MnO_2-electrode in nH_2SO_4 (molecular normal), and connect it by means of a small syphon tube with a vessel filled with $2n$ KNO_3 solution, in the other side of which the normal electrode similarly dips. Measure the E.M.F. by means of the compensation apparatus; the MnO_2 is the positive pole (corresponding to the PbO_2 electrode of the accumulator). The E.M.F., which is at first too small, quickly becomes constant (1·13—1·14 volts).

When the value is constant to 0·001 volt, remove the electrode from the nH_2SO_4 solution and immerse it in a $\frac{1}{10}n$ solution; again measure until approximately constant. The E.M.F. is now about 0·1 volt smaller than in the first case. The difference would be exactly 0·116 volt if the nH_2SO_4 contained exactly ten times as many $H^{\cdot}$ ions as the $\frac{1}{10}n$ solution. However, since the two solutions are not dissociated to the same degree, this is not the case. Their $H^{\cdot}$ ion concentrations are in the same ratio as their specific conductivities (according to Kohlrausch, 0·366 and 0·0428 at 18°). Calculate π according to these numbers (see above).

After the measurements have been completed add to the $\frac{1}{10}n$ solution of H_2SO_4 ten drops of concentrated $MnSO_4$ solution in two portions, first one, and then nine drops. Observe that the E.M.F. falls and that the difference between the two values is about 0·03 volt.

CHAPTER XII

ELECTROSTATICS

Fundamental Conceptions. Units.

The experiments hitherto have been concerned with current, or moving electricity, measured by means of its effect on a magnet in *electromagnetic* units. To define a quantity of electricity at rest in terms of its magnitude it is necessary to have recourse to other laws, and to employ other units of quantity, the *electrostatic* units.

According to Coulomb's law, two quantities of electricity E_1 and E_2 at a distance r, exert a force against one another of the magnitude $\frac{E_1E_2}{r^2}$. Since the dimension of a force in C.G.S. units is $[lmt^{-2}]$ the dimension of a quantity of electricity in electrostatic units is $[l^{\frac{3}{2}}m^{\frac{1}{2}}t^{-1}]$.

In electromagnetic units quantity of electricity is equal to current strength multiplied by time. The dimension of current strength results from the Biot-Savart law, that a small portion of current path (length l, current strength i) at distance r from a magnet pole M exerts a force of $\frac{iMl}{r^2}$. M, however, has the same dimension as the electrostatically measured quantity of electricity, since the analogous law holds for two magnet poles that the force exerted between them is $\frac{M_1M_2}{r}$.

Hence the amount of electricity in electromagnetic units

$$it = \frac{lmt^{-2} \cdot t \cdot l^2}{l \cdot l^{\frac{3}{2}}\, m^{\frac{1}{2}}\, t^{-1}} = [l^{\frac{1}{2}}m^{\frac{1}{2}}],$$

and the ratio between the dimensions of electrostatic and electromagnetic quantities of electricity is equal to lt^{-1}, the dimension of a velocity.

It is well known that a velocity of 300000 kilometres a second must be imparted to a ring in which is placed the electrostatic unit of electricity, in order that its electromagnetic effect may equal that of the electromagnetic unit. The velocity is that of light. The ratio between the two units is accordingly 300×10^8 cm/sec. Ten ampere-seconds, the C.G.S. unit of electricity measured electromagnetically, are equal to 300×10^8 electrostatic units.

Since unit quantity of electricity at unit distance exerts unit potential, the dimension of the potential V, measured electrostatically, is equal to $[l^{\frac{1}{2}}m^{\frac{1}{2}}t^{-1}]$, and the unit is 300 volts, since 1 volt is equal to 10^8 electromagnetic C.G.S. units.

If a conductor placed in a position of zero potential is charged to unit potential by unit quantity of electricity, it possesses unit **capacity**. The capacity $c = \frac{E}{V}$, and is therefore equal to the quantity of electricity with which the body is charged at unit potential. The dimension of the capacity is $[l]$.

Since 1 coulomb $= 3 \times 10^9$ and 1 volt $= \frac{1}{300}$ of the corresponding electrostatic C.G.S. units, the capacity of a conductor charged to a potential of one volt by 1 coulomb of electricity, a quantity termed 1 **farad**, is equal to 9×10^{11} [cm.] electrostatic C.G.S. units. The millionth part of this quantity is termed a microfarad (MF.). 1 cm. $= 1{\cdot}11 \times 10^{-6}$ MF.

Two conductors facing one another and completely insulated from each other form a **condenser**; the closer the plates are to one another the larger will be the capacity. It depends on the distance between the plates, their shape, and the nature of the insulating material between them.

If the air (or, strictly speaking, the vacuum) between two condenser plates is replaced by another substance, and the capacity of the system as a consequence is increased D times, then D, the ratio between the two capacities, is the *dielectric constant* (D.E.K.) of that substance. Thus D is a ratio, without dimension.

If two similar plates, each about f square centimetres in area, are placed opposite each other and parallel, and a cm. apart—where a is small relatively to their size—and if the insulating material between has the D.E.K. D, then the capacity of the condenser (Franklin's Plate) is $\frac{Df}{4\pi a}$. If the coating of a Leyden jar is h cms. high, its inner radius is r cms., and the thickness of the wall a, the capacity is $\frac{Dlr}{2a}$, where D, the D.E.K. of ordinary glass, lies between 5 and 6.

The amount of electricity contained by a condenser is proportional to its capacity c, and consequently to its D.E.K.; the amount passing through a conductor is directly proportional to its conductivity, inversely to its resistance. Hence *mutatis mutandis* a capacity c corresponds to a conductivity $1/r$. D has been designated the electrostatic conductivity. If two capacities c_1 and c_2 are in *parallel*, this effect is additive; if they are arranged in *series*, the total capacity is $\frac{c_1c_2}{c_1 + c_2}$, the inverse of the effect which takes place with resistances.

Comparison of Two Capacities.

Two capacities are compared most simply by the use of Wheatstone's arrangement for the measurement of resistances (see p. 127 and cp. the observations on lines of force, etc. p. 135). R and X are replaced by a known capacity, and that to be measured. If the circuit consists successively of the capacities c_1 and c_2, and the resistances r_2 and r_1, it is obvious that the telephone will be silent only when

$$c_1 : c_2 = r_2 : r_1.$$

The parts of a cylindrical bridge can be used as simple resistances; with well wound larger resistances a sharper minimum is obtained. It is highly important to use the best insulation attainable in all electrostatic measurements. Glass is in general insufficient. Ordinary glass must be coated with shellac. Only paraffin and sealing-wax, and, for the best apparatus, amber, are lasting insulators.

Exercise.—Compare a Franklin's Plate with 0·1 MF. or a smaller capacity; repeat with a large Leyden jar. Then compare the jar with the plate, and arrange plate and jar first in parallel, and then in series, and compare them with a known small capacity (preferably a second jar). Finally calculate the approximate capacity from the dimensions. (The D.E.K. of glass can be taken as 5.) 1 cm. = $1{\cdot}111 \times 10^{-6}$ MF. (see above).

Measurement of Dielectric Constants.

The most elegant method is based on the alteration of the capacity of a condenser when a liquid of unknown D.E.K. is added.

In principle it is sufficient to compare the capacity of the condenser filled with air, and with liquid, with a constant capacity, by the bridge method. However, the very small conductivity of the liquid becomes perceptible.

In order to eliminate the conductivity and to enable measurements to be made, Nernst has improved the bridge method. The two resistances are made equal; two condensers can be so changed that the alteration of their capacity is known, and a third is filled first with air, then with the liquid whose D.E.K. is to be measured, and arranged in parallel with each of the other condensers in turn. Further, two measurable variable resistances are arranged in parallel with the two comparison condensers. The telephone will be completely silent only when the capacities of the condensers, as well as the resistances, are equal.

In order to have symmetrical resistances which can be altered conveniently, all four consist of badly conducting liquids; the liquid usually employed, the so-called *Magnanini's solution*, has a very small temperature coefficient. (It is an aqueous solution of 121 grams of mannitol, 41 of boric acid, and 0·06 of potassium chloride in a litre.) The electrodes are well-platinised platinum wires, or small pieces of foil. One electrode in each pair can be moved micrometrically; the electrodes of those resistances which serve to balance the conductivity of the liquid are movable in a measurable manner. They consist of glass tubes of the form The two vertical limbs are of different width. The wide tube with relatively larger electrodes is used to balance a large conductivity; for smaller conductivities the capillary tube is sufficient; the third electrode, a small strip of platinum foil, always remains immersed in the horizontal limb.

The variable condensers consist of two well-insulated brass plates, fixed parallel to each other, between which a glass plate can move parallel to both, and to a measureable degree. A millimeter scale is fixed to the groove along which the glass plate moves, and the displacement is read by means of a vernier fixed to the plate itself. As the glass plate is pushed into the condenser the capacity is raised. The apparatus is standardised with a liquid of known D.E.K., so that a displacement of one millimetre can be used as an arbitrary unit. One plate condenser is calibrated with a constant capacity, namely, with the air-filled condenser, which afterwards contains the liquid. This consists of a circular nickel vessel with ebonite cover, through which a nickel tube passes, and can be moved with difficulty. To the end of the nickel tube is brazed a nickel plate, which completely fills the circular section of the trough. To the underside of the plate is cemented a small piece of glass about a millimetre thick, by means of which the nickel plate can be fixed in position. If the nickel plate is forced so low that the small piece of glass rests on the bottom of the trough, the capacity becomes a sharply defined quantity. It corresponds to a displacement of about 1 cm. of the glass plate in the measuring condenser. A small thermometer can be placed in the nickel tube. For substances having a larger D.E.K. a small electrode is used, further removed from the bottom.

Finally, to obtain a high frequency current, Nernst has introduced an induction coil, possessing a more rapid interrupter, which, in place of the ordinary stiff and noisy make and break instrument, consists of a half-stretched steel wire carrying a platinum contact. By changing the tension of the spring and inserting a suitable resistance the sound can be damped to a low rattle, which produces but a slight hum in the telephone, so that the ear is not annoyed.

The insulation of all parts of the apparatus must be made as perfect as possible. For this purpose the back of the telephone has a wooden shell, and if necessary it must also be covered with a coat of sealing-wax. The liquid condenser is placed on a paraffin block.

Since every wire becomes charged and acts as a condenser, and the capacity of a system depends on the relative position of the parts, any bending or other displacement of the wires during a measurement must be avoided.

Figure 47 shows the arrangement quite schematically. J is the secondary coil of the induction machine, and to it are joined the two equal liquid resistances R_1 and R_2; N is the nickel trough, which by a small side displacement is joined first to the one, then to the other measuring condenser, C and C_1, arranged in parallel. The two wires by which connection is made should be short and arranged symmetrically. R_3 and R_4 are the variable liquid resistances, T the telephone. The telephone is silent when $C + N = C_1$, $R_1 = R_2$, and $R_3 + R_N = R_4$.

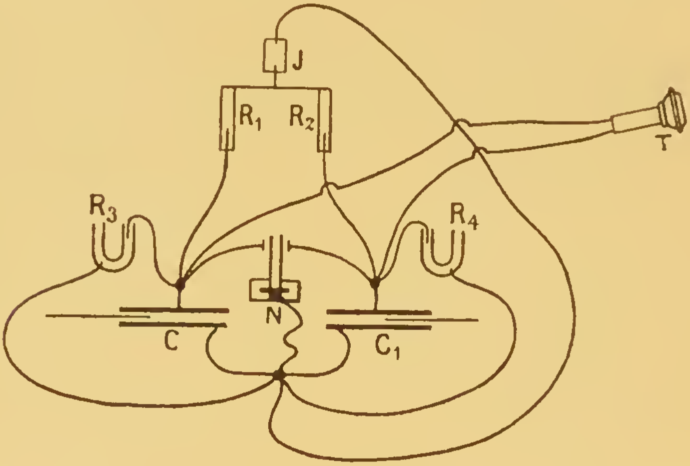

FIG. 47.

Method. 1. *Adjustment of the two equal resistances R_1 and R_2.*—N, R_3 and R_4, are removed from the circuit, and a commutator is arranged between R_1, R_2, C and C_1; R_1 and R_2 are made approximately equal, C any size, and C_1 adjusted until the telephone is silent; then the current is reversed. The number of millimetres through which the glass plate in C_1 has to be moved until the telephone is again silent is noted; the plate is moved back through half the distance, and either

R_1 or R_2 altered until the telephone is again silent, the current again reversed, and so on. By means of smaller and smaller screw rotations a position is found where a current reversal alters the minimum to less than 0·1 mm. No part of the apparatus must be displaced by a greater amount during the whole measurement.

2. *Calibration of one Measuring Condenser.*—N is brought between the two wires connecting C and C_1, the glass plate in C_1 is fixed at zero, and that in C adjusted until the telephone is silent; then N and C_1 are arranged in parallel, and the displacement of C_1 necessary for silence is measured. The plate in C_1 is placed at 1, 2, 3 cm. respectively, and in this way the scale is calibrated. The displacements should always be equal. The deviation from the mean values is plotted on squared paper for the part of the scale affected, and is afterwards applied to each reading.

3. *Standardisation of the Condenser N.*—R_3 and R_4 are brought into the circuit, and so arranged that the minimum sound is very sharp. N is arranged in parallel first with C, then with C_1; the (corrected) half displacement of C corresponds to the capacity of the empty trough plus the connections; into N are poured 2 c.c. of a standard liquid (benzene $D_{17^\circ} = 2{\cdot}26$; metaxylol $D_{25} = 2{\cdot}36$, pure ethyl ether, $D_{20} = 4{\cdot}27$) and it is again measured. If the minimum is uncertain, the solution conducts perceptibly, and R_3 and R_4 are altered respectively, until the minimum is sharp; C_1 is again moved until the telephone is silent, and the minimum improved by alteration of the resistances. By ever decreasing alterations of C_1 and the resistances R_3 and R_4 it is possible to render the minimum extremely sharp.

Let the half displacement right and left for the parallel position be S_0.

Several measurements are always made at the different positions of the condenser C.

4. *Estimation of the D.E.K. of Toluol.*—Two c.c. of toluol are poured into the trough and measured as just described. Let the half displacement be S.

Calculation.—If the capacity of the trough is c, that of the connections c', the D.E.K. of the standard liquid D_0, that of toluol D, then the following ratios correspond, $s : (1 \,.\, c + c')$; $S_0 : (D_0 c + c')$; $S : (Dc + c')$; whence

$$D = (D_0 - 1)\,\frac{S - s}{S_0 - 1} + 1.$$

If $D > 5$, a platinum crucible with smaller electrodes, is used, and is standardised with aniline ($D_{18} = 7{\cdot}2$) or acetone ($D_{19^\circ} = 20{\cdot}7$).

Remarks.—The trough or the crucible must be emptied immediately after use, since the organic liquids used (especially benzene) soften and swell the ebonite coating. The substances must be pure, and freed from water especially, since its D.E.K. is very high (about 81).

For the measurement of solids the suspension method is suitable (see pp. 35 and 79).

The D.E.K. of a substance is equal to the square of the index of refraction for infinitely long waves, and good constancy should be obtained if D is substituted in the formula for molecular refraction (see p. 76). The relation does not hold generally, especially for substances containing hydroxyl groups, which absorb long waves strongly.

The parallelism between the D.E.K. of a liquid and its dissociating power, which has recently been proved for a large number of substances, is very important for the physical chemist.

The D.E.K.s of the ordinary solvents are, in round numbers, water 81, methyl alcohol 32, ethyl alcohol 26, amyl alcohol 16, ethyl ether 4, benzene 2. The order of ionising power of these solvents is the same.

The Quadrant Electrometer.

The quadrant electrometer consists of four flat metal quadrants, arranged in a circle with air spaces separating them; there are thus two vertical air channels at right angles to each other. Opposite quadrants are connected by conducting wires. In the centre of the arrangement swings a very light metallic needle on an extremely thin conducting fibre, which also carries a light mirror; the fibre is either a hair-drawn platinum wire, or a very thin silica fibre made conducting by a solution of calcium chloride. When the needle is at rest, it should lie parallel to one of the quadrant divisions; this can be brought about by turning the torsion head on the copper head of the instrument. If one pair of quadrants is charged to a potential $+ Q$, the other pair to a potential $- Q$, and the needle to the potential X, then the needle will be repelled through an angle proportional both to the charges on the quadrant pairs and to its own charge. The charging is done by connecting the pairs with a series of cells, *e.g.*, small dry cells, the middle of the series being kept at zero potential by *earthing* it, *i.e.*, by connecting it metallically to the earth (water-pipe or gas-pipe).

The insulation of the quadrants and needle must be perfect. The *needle* consists of silver foil; readings are made by Poggendorff's method. The instrument can be calibrated with normal elements.

The velocity of the needle deflection is proportional approximately to its charge X. This should be sufficiently great to produce a deflection of several cms. on the scale; the time taken to pass 2, 5 or 10 scale divisions is measured with a stop-watch, but it should first be observed whether the velocity in the part of the scale employed is constant, *i.e.*, that the time and deflection are proportional to each other. It is therefore better to work with not too great deflections. The sensibility can be changed by putting a capacity in parallel.

Comparison of the Radioactivities of Uranium Pitchblende and a Radiferous Barium Salt.

The element *radium* is the highest known member of the barium group, and has an atomic weight of about 226. Minute traces are contained in all uranium ores and salts; these continually disintegrate, sending out α, β and γ rays. The α rays are particles of some kind of matter holding an electric charge, and travelling with an enormous velocity; the β rays are *electrons*, while the γ rays consist of ether vibrations, somewhat resembling X-rays. All these *ionise* air, *i.e.*, make it conduct electricity. If a radioactive body is placed on a charged plate, opposite which is another similar plate, at first earthed and then metallically connected with the electrometer needle, the second plate, immediately earthing is suspended, becomes charged to an extent which is measured by the deflection of the needle, and is proportional to the radium content of the active body. In this way the quadrant electrometer can be used to measure quantitatively quantities of substance which are far too small to be detected by ordinary analytical methods.

Equal quantities of finely powdered uranium pitchblende and of a slightly radioactive barium salt are placed in flat weighing bottles of the same height and diameter, so that in both cases the bottom of the bottle is just covered. Each vessel, uncovered, is placed in turn on a circular piece of zinc plate, charged to 110 volts, and standing on a paraffin block. It is surrounded by a glass ring (for which purpose a beaker with the bottom removed or the shade of an inverted incandescent burner can be employed), which has a layer of tinfoil inside and outside, both tinfoil rings being earthed. On the glass ring rests the second plate connected with the needle. The plate containing the powder is kept at a high voltage by connecting it to one pole of a main, while the other is earthed. It is useful to insert in the connection to the main a fibre saturated with calcium chloride solution, which serves as a fuse. The diagram (Fig. 48) shows the various connections. Z_1 and Z_2 are the zinc plates, R is the glass ring which separates them; a, b, and c, are the holes of a mercury contact-breaker. If a and b are connected, then plate Z_2 and the needle are earthed; if the connection is interrupted by shifting the contact-maker to c, then when Z_1 is connected with the high voltage battery, and a radioactive substance is placed between Z_1 and Z_2, Z_2 and the needle become charged.

If the electrometer is too sensitive, a capacity C is placed in parallel *; if C' is the capacity of the electrometer, the sensitiveness is reduced in the ratio $\frac{C'}{C' + C}$; if C' is small in comparison with C, the sensitiveness is inversely proportional to the added capacity. By comparing it with a known capacity of the same magnitude (a Leyden jar) C' can be measured electrometrically.

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* Capacities should be insulated on paraffin blocks.

It is necessary at the commencement of the experiment to make certain that the air of the room has no appreciable conductivity. Plate Z_1 is charged to 110 volts, Z_2 is earthed, the earthing is suspended, and the time for a deflection of 1 cm. taken several times (mean reading 25 seconds, say). Z_2 is again earthed, as a precaution the 110 volts are switched off, the pitchblende placed on Z_1, and a measurement taken as before (time for 1 cm. say 1·0 seconds). The pitchblende is removed and the radium barium salt takes its place, with a capacity of 0·2 (say) microfarad placed in parallel. By measuring as before, the time of deflection is found to be 30·7 seconds per cm. If the capacity C' is 0·00012 MF. it follows that without the 0·2 MF. the time would be

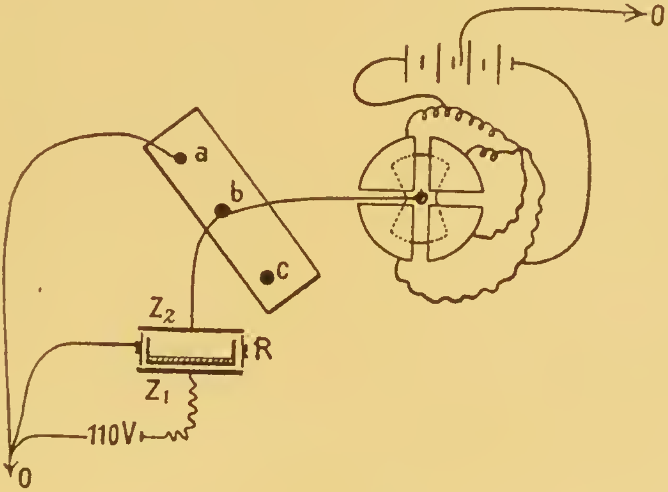

FIG. 48.

$$\frac{30·7 \times 0·00012}{0·20012} = 0·0184 \text{ seconds for 1 cm. deflection.}$$

The conductivities are inversely proportional to the times. They are in the above example for air 1/25 = 0·04, for pitchblende, uncorrected, 1, and for the radium preparation, uncorrected, 1/0·0184 = 54·4. If we correct for the conductivity of the air (*i.e.*, the *natural leak*), the conductivities of the pitchblende and the radium preparation are, respectively, 0·96 and 54·4. The latter is therefore 56·6 times as active as its parent substance.

It is advisable to measure the weaker substance first, so that the air is not ionised more than necessary during the measurement, and that the corrections do not become too large and uncertain.

The capacities are altered when measuring stronger substances.

APPENDIX

Comparison of Radioactive Substances by an Electroscope.

The radioactivities of different substances can be compared easily and quickly by means of an *electroscope*. The principle is the same as that with the electrometer. A rough electroscope can be constructed, with simple materials, which will give fairly accurate results.

For this purpose a tin canister, some four or five inches in diameter, is taken, and two small mica windows are inserted in it at the same height and diametrically opposite each other. They are fastened to the tin with sealing-wax. The bottom of the vessel must be made removable. The neck is closed by a cork covered with sulphur as insulation. The interior arrangement is shown diagramatically in Fig. 49.

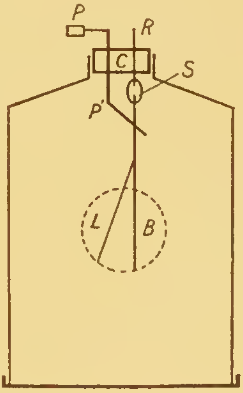

FIG. 49.

The cork is penetrated by a rod *R*, supporting a ball of sulphur *S*. This in its turn supports, and at the same time insulates, a brass rod *B*. To *B* is attached a strip of aluminium leaf *L*. (It can be caused to adhere by moistening the surface of the brass, and pressing the aluminium leaf against it.) Through the cork also passes a second metal rod *PP′*, with a handle of ebonite or sealing-wax. By rotation this rod can touch *B*, and it is so used to charge the leaf system. While in contact with *B*, its free end is touched with a charged rod of sealing-wax; *P* is then revolved to break the earth contact with *B* and *L*. *R* and the containing vessel should be earthed throughout, and *P* also finally earthed, so that the leaf system only is charged.

The charged leaf L is repelled through a considerable angle. It slowly falls; the rate of fall is observed through a short-focus telescope, in which is inset a good glass scale. The dotted circle indicates the position of the windows in the vessel, and the part of the leaf system observed through the telescope. It must be illuminated by a constant source of light, preferably an electric lamp screened with semi-transparent paper or glass, and placed in alignment with the windows and telescope. The whole is conveniently arranged in a dark room.

The slow fall of the leaf under ordinary conditions is due to the ionisation of the air, and is termed the *natural leak* of the electroscope. With good insulation the leaf should take at least half a minute to pass over a degree of arc.

Exercise.

Determine the natural leak of an electroscope. Several consecutive readings should agree closely. Express the mean result in the fraction of a scale division passed over per second. (Observe whether the leaf traverses different parts of the scale at the same rate; if not, then it is obvious that a definite part must be used, preferably the middle portion.) Remove the bottom of the electroscope, and place on it a glass dish* similar to those used in the previous experiments (p. 182) but empty. Replace it and redetermine the leak of the instrument. Then substitute for the empty dish that which contains the powdered pitchblende used in the last experiment. Measure the rate of fall of the leaf. It will be much greater. Several consecutive readings must be taken over a considerable portion of the scale. Replace the pitchblende by the radium-barium salt, and take a fresh series of observations (over the same portion of the scale). Express the mean result in both cases in terms of the number of scale divisions passed over per second. Subtract from each value the natural leak (obtained with the empty glass or metal vessel in the system). The radioactivities are inversely proportional to the times of fall, directly proportional to the rate of discharge. (What is the difference between the two radioactivities due to?)

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* In these and the preceding experiments small flat metal dishes are preferable, as less likely to hold small charges of electricity.

For the radium-barium salt it may be convenient to substitute equal weights of finely-powdered uranium salts. Select two of widely different molecular weights, as uranium oxide U_3O_8, and potassium uranyl sulphate. (If possible salts which have been prepared at least a year previously.) It should be shown that the radioactivity is proportional to the content of uranium, in these cases, but that the activity of pitchblende is four or five times greater than that of the oxide. To what is this excess of activity in the pitchblende due?

TABLE I.

The most Important Physical-Chemical Constants.

The volume of a gram-molecule of gas at 0 and 760 mm. is 22410 c.c.
The density of dry air at 0 and 760 mm. is 0·001293.
The mean molecular weight of air is 28·9.

$$\begin{aligned} R = \frac{P_0\,V_0}{273} \text{ (in C.G.S. units)} &= 0{\cdot}8317 \times 10^8 \text{ (ergs}\cdot T^{-1}\text{)}.\\ &= 1{\cdot}985 \text{ (gram-calories}\cdot T^{-1}\text{)}.\\ &= 0{\cdot}0821 \text{ (litre-atmosphere}\cdot T^{-1}\text{)}.\\ &= 0{\cdot}861 \times 10^{-4} \text{ (watt-second}\cdot T^{-1}\text{)}.\end{aligned}$$

1 erg = $238{\cdot}7 \times 10^{-10}$ g. cal.
1 g. cal. = $0{\cdot}4188 \times 10^8$ ergs.
1 volt-ampere per second = 10^7 ergs = 1 watt-second = 0·2387 g. cal.
1 ampere per second = 1 coulomb deposits 1·118 mg Ag.
0·3294 mg Cu (from cupric salts).
sets free 0·1740 c.c. Knallgas at 0° and 760 mm.
96540 coulombs deposit a gram equivalent.

TABLE II.

Specific Gravity and Vapour Pressure of Water.

Temperature.	Density.		Pressure in mm.		Temperature.	Density.		Pressure in mm.	
0°	0·99987		4·58		22°	0·99780		19·66	
							24		122
4°	1·00000		6·09		23°	0·99756		20·88	
							24		130
8°	0·99988		8·02		24°	0·99732		22·18	
							25		137
10°	0·99973		9·18		25°	0·99707		23·55	
							26		144
12°	0·99953		10·48		26°	0·99681		24·99	
		13		71			27		152
13°	0·99940		11·19		27°	0·99654		26·51	
		13		75			28		159
14°	0·99927		11·94		28°	0·99626		28·10	
		14		79			29		169
15°	0·99913		12·73		29°	0·99597		29·79	
		16		84			30		177
16°	0·99897		13·57		30°	0·99567		31·56	
		17		88					
17°	0·99880		14·45		35°	0·99406		41·85	
		18		93					
18°	0·99862		15·38		40°	0·99224		54·97	
		19		99					
19°	0·99843		16·37		45°	0·99025		71·50	
		20		104					
20°	0·99823		17·41		50°	0·98807		92·17	
		21		109					
21°	0·99802		18·50						
		22		116					

TABLE III.

Reduction of the Barometer Height to 0° C.

	Glass Scale.				Brass Scale.			
Temperature.	740 mm.	750 mm.	760 mm.	770 mm.	740 mm.	750 mm.	760 mm.	770 mm.
10°	1·28	1·30	1·31	1·33	1·21	1·22	1·24	1·26
12°	1·53	1·56	1·58	1·60	1·45	1·47	1·49	1·51
14°	1·79	1·81	1·84	1·86	1·69	1·71	1·73	1·76
16°	2·05	2·07	2·10	2·13	1·93	1·96	1·98	2·01
18°	2·30	2·33	2·36	2·39	2·17	2·20	2·23	2·26
20°	2·56	2·59	2·62	2·66	2·41	2·44	2·47	2·51
22°	2·81	2·85	2·89	2·92	2·65	2·69	2·72	2·76
24°	3·06	3·11	3·15	3·19	2·89	2·93	2·97	3·01
26°	3·32	3·36	3·41	3·45	3·13	3·17	3·21	3·26

TABLE IV.

The Atomic Weight and other Constants of the most important Elements.

Symbol.	Atomic Weight 0 = 16.	Specific Gravity in solid form at room temperature.	Specific Heat in solid form at room temperature.
Ag	107·88	10·50	0·056
Al	27·1	2·60	0·21
Ba	137·37		
Br	79·92		
C	12·00	Diamond 3·52 Graphite 2·3	0·12 0·17
Ca	40·09		
Cd	112·4	8·64	0·055
Cl	35·46		
Cu	63·57	8·93	0·093
Fe	55·85	7·6 – 7·9	ca. 0·11
H	1·008		
Hg	200	(liq.) 0° 13·596 20° 13·546	(liq.) 0·033
I	126·92		
K	39·10		
Mg	24·32		
Mn	54·93		
N	14·01		
Na	23·00		
Ni	58·68	8·9	0·11
O	16·00		
Pb	207·1	11·37	0·030
Pt	195·0	21·50	0·032
S	32·07	rhomb. 2·07 monocl. 1·96	rhomb. 0·16
Sn	119·0	White 7·29	0·055
Zn	65·37	7·1	0·093
Brass		ca. 8·4	0·093
Glass		ca. 2·5	0·19

TABLE V.

Mobilities of some Ions at 18° (in round numbers) and their Temperature Coefficients.

$H^{\cdot}$	313	0·015	OH'	172	0·018
$K^{\cdot}$	65	0·022	$\frac{1}{2}SO_4''$	68	0·023
$NH_4^{\cdot}$	64	0·022	Cl'	65	0·022
$Ag^{\cdot}$	55	0·023	NO_3'	61	0·021
$Na^{\cdot}$	44	0·024	$CH_3.COO'$	33	0·024

TABLE VI.

Molecular Conductivities.

Dissolved Substance.	$t°$.	v.	Λ.
HCl	18°	1	301
		10	351
		100	370
Monochlor-acetic acid.	25°	16	56·6
		32	77·2
		128	137·0
		256	176·8
		512	222·6
Malonic acid	25°	32	77·1
		64	103·6
		128	136·1
		256	174·8
Acetic acid	18°	1	1·32
		10	4·60
		100	14·3
,, ,,	25°	8	4·63
		32	9·2
		128	18·1
		256	25·4
		512	34·3
NaOH	18°	1	157
		10	195
		100	203

Dissolved Substance.	$t°$.	v.	Λ.
NH_4OH	18°	1	0·89
		10	3·3
		100	9·6
NH_4Cl	18°	1	97·0
		10	110·7
		100	122·1
NaCl	18°	1	74·4
		10	92·0
		100	102·0
$AgNO_3$	18°	1	67·6
		10	94·3
		100	107·8
Silver Acetate	25°	143	95·9
		333	99·0
Na-Acetate	18°	1	41·2
		10	61·1
		100	70·2
Na-Monochlor-acetate.	25°	32	78·4
		64	81·7
		128	84·1
$\frac{1}{2}ZnSO_4$	18°	1	26·2
		10	45·3
		100	72·8

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